

JPRS-UCH-84-005

3 May 1984

USSR Report

CHEMISTRY



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CHEMISTRY

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CYTISINE DEMETHYLATION

Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 5, Sep-Oct 83
(manuscript received 10 Jan 83) pp 43-45

KASYMOV, T. K., ISHBAYEV, A. I., DANIL'CHUK, D. N., and YUSUPOV, SH.,
Institute of Bioorganic Chemistry, Uzbek SSR Academy of Sciences

[Abstract] In order to recover alkaloids that are often discarded as by-products, studies were conducted on the demethylation of cytisine. The experimentally-determined conditions that favored optimum cytisine demethylation involved reaction with MnO_2 in 30% acetic acid over a water bath for 2-2.5 h, addition of 30% NaOH and extraction with chloroform. TLC on aluminum oxide revealed that the product mixture consisted of three components: cytisine (30%), methylcytisine (40%) and a product (12%) with $R_f = 0.65$.

References 8: 7 Russian, 1 Western.
[136-12172]

UDC 615.356:577.164.14].074:543.544

GAS-CHROMATOGRAPHIC ASSAY OF PANTOIC ACID IN VITAMIN-CONTAINING PREPARATIONS

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian No 12, Dec 83
(manuscript received 7 Jan 83) pp 1513-1516

SLYSHENKOV, V. S. and MOYSEYENOK, A. G., Coenzyme Laboratory, Department of Regulation of Metabolism, BSSR Academy of Sciences, Grodno

[Abstract] Development of a method of hydrolysis of calcium D-pantothenate, D-pantenole and D-pantethine which ensures quantitative formation of pantolactone from ampule samples of pantothenate-containing compounds and a method of quantitative chromatography of pantolactone on a Soviet chromatograph was described and discussed. The procedure provided complete hydrolysis of the compounds within 105 minutes at 80°C. Relative error with a confidence factor of 0.05 does not exceed ± 1.5 percent. Figures 2; references 6: 2 Russian & Western.
[110-2791]

UDC 537.525+546.12

MECHANISM OF FORMATION AND DISINTEGRATION OF ACTIVE PARTICLES IN HALOGEN PLASMA

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY:KHIMIYA I KHIMICHESKAYA TEKHNLOGIYA in Russian Vol 26, No 12, Dec 83 (manuscript received 22 Oct 81) pp 1441-1445

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[Abstract] Analysis is reported of mechanisms of formation and disintegration of charged and neutral active particles for low pressure discharges in chlorine, bromine and fluorine under the conditions of gas pressure from 10 up to 1000 Pa, power input into the discharge of 0.1-10 W/cm³ and typical size of the plasma containing vessel of 0.1-10 cm. The study was done to determine optimum regimes of halogen plasma combustion. The analysis proceeded from the study of balances of formation and disintegration of free atoms in the charged particles.

This balance was determined by the following processes: ionization of molecules, ionization of atoms, attachment of electrons to molecules, volumetric ion-ion recombination, diffusion of electrons and positive ions by the walls, heterogeneous recombination of the atoms and volumetric recombination of the atoms. References 35: 17 Russian, 18 Western.
[131-2791]

UDC 541.1:621.365.52

FEATURES OF THERMAL DECOMPOSITION OF SODIUM BICARBONATE EXPOSED TO HIGH-FREQUENCY ELECTRIC FIELD

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNOLOGIYA in Russian Vol 26, No 12, Dec 83 (manuscript received 13 Jul 81) pp 1453-1456

BERDOV, G. I., VOLKOVA, L. M., VOLCHENKOVA, N. A. and LINNIK, S. I.,
Department of Chemistry, Novosibirsk Engineering Construction Institute

[Abstract] Study of the action of a high-frequency electric field on the thermal decomposition reaction of sodium bicarbonate involved comparison of NaHCO_3 in a thermostat and under the effect of a high-frequency electric field (40.68 MHz). It was found that the electric field accelerates sodium bicarbonate decomposition significantly. In addition to the heat effect of the electric field there may also be a local effect on the reactive part of the solid due to absorption of the energy field by it. Figures 4; references 8: 7 Russian, 1 Western.
[131-2791]

UDC 677.494.674+677.042.5:66.062.5+543.544.25+541.183

GAS CHROMATOGRAPHIC ANALYSIS OF ADSORPTION OF ORGANIC SOLVENTS TO POLYESTER FIBERS

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNOLOGIYA in Russian Vol 26, No 9, Sep 83 (manuscript received 6 Jan 82) pp 1110-1113

ARZHAKOVA, T. I. and BLINICHEVA, I. B., Chair of Chemical Technology of Fibrous Materials, Institute of Nonaqueous Solvents, USSR Academy of Sciences; Ivanovo Institute of Chemical Technology

[Abstract] Gas chromatography was employed to study the adsorption of anisol, tetrachloroethane and trichloroethylene vapors to the polyester fibers lavsan (Dacron) and shelon-2. Evaluation of the adsorption isotherms showed that adsorption decreased in the following sequence to the polyester fibers: anisol>tetrachloroethane>trichloroethylene. In addition, for the temperature range 65-100°C calculations were also made of the full heat of adsorption, heat of condensation, and heat of interaction. Figures 1; references 5 (Russian).
[130-12172]

DETERMINATION OF DEHYDROGENASE ACTIVITY OF MICROORGANISMS IN ACTIVE SLUDGE

Moscow PLASTICHESKIYE MASSY in Russian No 12, Dec 83 p 44

FRIDMAN, R. A. and RUDNENKO, Ye. V.

[Abstract] Quality control measures at water purification stations require determination of dehydrogenase activity, which is based on development of a stable color during transition from the oxidized to reduced state. One of the more sensitive indicators for this test is 2,3,5-triphenyltetrazolium chloride. Laboratory-based experiments were performed trying to improve the above test. Ascorbic acid was used as the reducing agent, butanol as the solvent. Average relative error of the test was 2.4%, sensitivity was 0.005 mg per test sample. Dehydrogenase activity of eight samples of sludge gave values ranging from 4.25 to 4.6 (average 4.40). References 2 (Russian).
[108-7813]

MASS SPECTROMETRIC STUDY OF THERMAL STABILITY OF ARTIFICIAL MICAS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 274, No 1, Jan 84
(manuscript received 20 Apr 83) pp 84-87

ANIKIN, I. N., RAT'KOVSKIY, I. A., ASHUYKO, V. A. and ASNOVICH, E. Z.

[Abstract] This work determines the temperature at which decomposition of specimens of various micas begins, the composition and pressure of vapor above the specimens, and the temperature at which liberation of individual vapor components begins. Studies were performed on a mass spectrometer modified for high temperature measurements. All specimens were studied as powders with particle size 0.4-1 mm prepared by crushing of mica plates obtained by spontaneous crystallization. For comparison, single crystal specimens of normal fluorophlogopytes were studied as plates 8 mm in diameter, thickness 30-60 μ m, obtained by both spontaneous and oriented crystallization from melt. The micas studied can be arranged in order of decreasing thermal stability as follows: Ba-FP, FP-plates, Pi-FP, V-FP, FP-powder. Figures 1; references 15 (Russian).
[122-6508]

THERMAL TRANSFORMATIONS OF HYDROCARBONS AT HIGH PRESSURES

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 274, No 1, Jan 84
(manuscript received 26 Apr 83) pp 100-102

VORONOV, O. A., GAVRILOV, V. V., ZHULIN, V. M., RAKHMANINA, A. V.,
KHLYBOV, Ye. P. and YAKOVLEV, Ye. N., Institute of High Pressure Physics,
USSR Academy of Sciences, Troitsk, Moscow Oblast; Institute of Organic
Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow

[Abstract] Results are presented indicating that full graphitization at high pressure and relatively low temperature is a rather common phenomenon in various types of hydrocarbons. Experiments were performed in a toroid type high pressure apparatus. Tablets 4.5 mm in diameter and 4 mm high were pressed of the organic compound tested and placed in a graphite crucible through which an electric current was passed. A pressure of 8 GPa was created at room temperature and the temperature was raised. Specimens were studied after extraction from the pressure apparatus at atmospheric pressure. Specimens included anthracene, diphenyl, paraffin, polyethylene, tolane, coal and oil sands. All specimens studied yielded graphite in the experiment. Figure 1; references 6 Russian.
[122-6508]

UDC:541 15+547.458.81+678.019.3

RADIATION-THERMAL DESTRUCTION OF CELLULOSE

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 274, No 1, Jan 84
(manuscript received 14 Apr 83) pp 102-106

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Institute of Physical Chemistry, USSR Academy of Sciences, Moscow; Institute
of High Molecular Weight Compounds, USSR Academy of Sciences, Leningrad

[Abstract] A study is presented of the effect of ionizing radiation on cellulose at elevated temperatures in order to accelerate the process of its destruction. Wood fiber cellulose with initial degree of polymerization 950, content of α -cellulose 99.1% was used. The cellulose was irradiated in sealed ampules in air or in a vacuum using a ^{60}Co γ -ray source. Dose power was 20kGr/hr, with experiments at high temperature (303-433K) performed in a thermostat. A previously described method of statistical analysis of the process of destruction of the polymer was used to produce a quantitative description of the experimental data obtained. As the temperature of γ -irradiation increased, the rate of destruction also increased significantly. γ -irradiation at elevated temperatures thus stimulates the process of destruction of cellulose and the formation of carbonyl and carboxyl groups. Figures 3; references 12: 8 Russian, 4 Western.
[122-6508]

BIOLOGICAL ROLE AND TOXIC PROPERTIES OF CYANIDES

Moscow PRIRODA in Russian No 12, Dec 83 pp 13-20

[Article by G. I. Oksengendler]

[Text] Gdal' Iosifovich Oksengendler, Candidate of Medical Sciences, is a member of the Main Health Administration of the Leningrad City Executive Committee of the Soviet of People's Deputies. He studied the effects of toxic substances on the organism and methods of controlling toxic effects. His articles were often published in the journal PRIRODA. He is the author of the book "Yady i protivoyadiya" [Poisons and Antidotes], Moscow, 1982.

In spite of the fact that cyanides¹ have been known since time immemorial, the significance of these chemical compounds is still sufficiently great in our days. Due to their high chemical activity, cyanides are used widely today in various sectors of industry (galvanoplastics, production of many synthetic materials, etc), in agriculture (fertilizers, chemical weed and pest killers, stimulators of plant growth), as well as in scientific studies.

In this article, we shall attempt to characterize the biochemical aspects of the cyanide problem. For this purpose, we shall examine the toxic properties and the mechanism of the effects of substances of this class on the organism, the molecular essence of the antidotal effect of anticyanide preparations, analyze the ways of the participation of cyanides in the primary synthesis of biomolecules, as well as evaluate their significance as radioprotectors and normal metabolic products.

Cyanide Around Us

Even ancient Egyptian priests knew how to prepare an essence from peach leaves which they used to kill people who committed an offense. In Paris, at the Louvre, there is a papyrus roll with the warning: "Do not utter the name of Iao under the threat of punishment by the peach". The following inscription was found in the temple of Isis: "Do not open, or you will die from the peach".

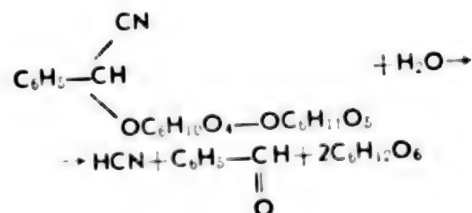
Now we know that hydrocyanic acid² forming in the process of fermentative transformations of some compounds of plant origin was the toxic substance.

Cyanides are familiar to us as chemical agents used in chemical warfare against large numbers of people: during the First World War, the French army used hydrocyanic acid as a poisoning substance; in Hitler's death camps, the fascists used poisonous cyclic gases (esters of cyanomethanoic acid); American troops in South Vietnam used highly toxic organic cyanides against the peaceful population. There is information that hydrocyanic acid is used in the United States in gas chambers for executing death sentences.

Hydrocyanic acid was first obtained in its pure form in the 1780's by the Swedish pharmacist and chemist Karl Schelle, who himself allegedly became a victim of this poison during one of his experiments. Thereafter, many prominent scientists studied the chemical structure, methods of production and applications of cyanide compounds. Hydrocyanic acid and its salts started being produced industrially only at the end of the last century, when an effective method of extracting gold and silver from ores with their aid was found.

Particularly large amounts of hydrocyanic acid (tens of thousands of tons) are used for industrial synthesis of acrylonitrile (a raw material in the production of synthetic rubber) and acetone cyanohydrin, which is necessary for the production of polymers and, specifically, of organic glass⁴. In many industrial processes, hydrocyanic acid is liberated in a gaseous state or forms when cyanides come in contact with other acids and moisture. All this creates a serious danger of intoxication.

Poisoning by cyanides is possible also when eating large amounts of seeds (kernels of fruit stones) of bitter almonds, peaches, plums, apricots, cherries, apples, bird cherries and many other plants of the rose family which contain glycoside amygdalin. Under the effect of the enzyme emulsin, this glycoside is decomposed in the organism to yield hydrocyanic acid:



Shelled bitter almonds contain (in combination with emulsin) the largest amount of amygdalin: up to three percent of their weight; apricot kernels contain somewhat less (about two percent). Approximately 100 shelled apricot kernels constitute a lethal dose of amygdalin (one gram). Just as amygdalin, hydrocyanic acid is separated by plant glycosides -- linamarin contained in flax and laurocerasin isolated from the leaves of the cherry laurel. Young bamboo shoots contain a large amount of hydrocyanic acid. It is known that the lethal dose of hydrocyanic acid for man is 1 mg/kg of the body weight; the toxicity of its salts -- potassium and sodium cyanides -- is approximately one third of that.

Hydrogen Cyanide and Origination of Biomolecules

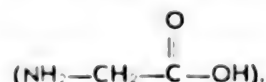
More than half a century ago, A. I. Oparin advanced a hypothesis according to which the origin of life began with the synthesis of the simplest compounds. At that time, it was already postulated that the atmosphere covering the lifeless ocean and the rocky surface of the earth contained at least four substances: water vapors, ammonia, methane and hydrogen. The existing notions of the chemical transformations of these simple molecules make it possible to recreate the picture of the formation of new compounds from them: hydrocyanic acid and formaldehyde, from which, in turn, components of the macromolecules of live organisms can be synthesized. It is in these reactions of the formation and subsequent transformations of hydrocyanic acid and formaldehyde that we should seek the clue to the appearance of the basic carriers of life: proteins and nucleic acids. Hydrocyanic acid forms under the effect of ultraviolet radiation from methane and ammonia:



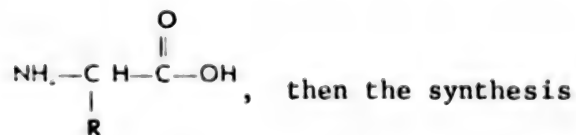
and formaldehyde forms from methane and water:



Each of these reactions includes several intermediate stages at which the molecules of the initial substances transform, producing methyl, hydroxyl and amino groups, as well as activated hydrogen. The initial and final products of these two reactions are now considered to be a necessary material for the construction of the simplest amino acids. Thus, the probable mechanism of the synthesis of glycine is usually divided into three stages: first, methylene imine forms from formaldehyde and ammonia, which in its reaction with hydrocyanic acid produces aminonitrile, and then, glycine forms from it as a result of hydrolysis:

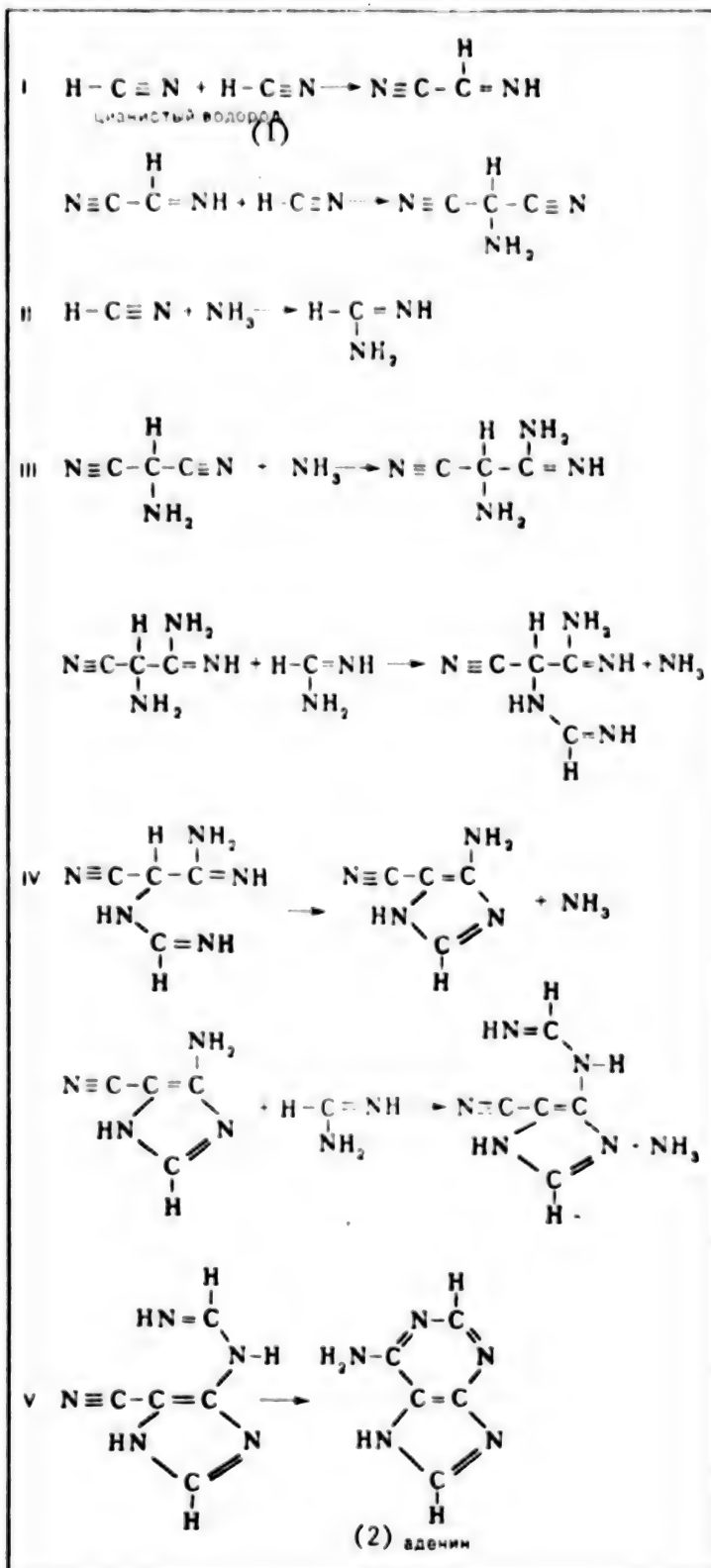


If we represent the structure of glycine in the form of



scheme of the remaining vitally important amino acids will become clear, since all of them are constructed on the same principle: for example, if $\text{R} = -\text{CH}_3$, then it is alanine, if $\text{R} = -\text{CH}_2\text{SH}$ -- cysteine, if $\text{R} = -\text{CH}_2\text{OH}$ -- serine, if $\text{R} = -\text{CH}_2\text{CH}_2\text{CONH}_2$ -- glutamine, etc.

Naturally, there arises a question: to what extent does this scheme of the abio-genetic synthesis of amino acids correspond to the events which occurred in the primary atmosphere of the Earth? The experiments conducted by S. Miller in 1953 at the University of California in the laboratory of H. Urey were one of the first proofs of its reality. In the course of a week, in a specially



Possible path of the synthesis of an adenine molecule from two molecules of hydrogen cyanide. Roman numerals show the sequence of reactions. Color indicates the products of intermediate reactions.

Key: 1. hydrogen cyanide
 2. adenine

constructed apparatus, a heated mixture of water vapors, methane, ammonia and hydrogen was subjected to the action of an electric discharge. Amino acids were found in the condensate, including glycine, alanine, and glutamic acid. This path of the formation of organic molecules was confirmed later by other experiments, and the presence of many "terrestrial" amino acids in a meteorite which fell in the territory of Australia in 1970 proves also their extraterrestrial existence.

As early as the beginning of this century, A. N. Bakh showed how considerably more complex organic compounds are formed from potassium cyanide and formaldehyde which can serve as a nutrient medium for microorganisms.

However, it seems that the possible role of hydrogen cyanide in the primary synthesis of the nitrous components of nucleic acids is particularly significant. And although the existing scheme of the probable synthesis of adenine is still hypothetical, the fact that one molecule of adenine (empiric formula $C_5H_5N_5$) quantitatively corresponds to five molecules of hydrogen cyanide speaks for itself.

Thus, the abiogenetic synthesis of a number of molecules constituting the chemical basis of vital activity necessarily includes a cyanide compound as the most important component of primary reactions of organic synthesis.

It is interesting that cyanides are common products of the normal metabolism of man and many species of animals: they were detected in biological fluids, in the expired air and in urine. Evidently, cyanide compounds form in the processes of the transformation of some macromolecules, primarily molecules of chromoproteins (their normal level in the blood plasma can reach 14 $\mu\text{g}\%$); the first to be mentioned among them is cyanocobalamin (vitamin B₁₂) which as is known, is necessary for normal hemopoiesis, functioning of the nervous system and the liver. Probably, it is not accidental that the liver of man and animals has a strictly specific enzyme, rhodanese, which is intended for neutralizing cyanide.

However, nature also assigned another role to cyanide: the role of a toxic substance with a pronounced selective effect on biological structures. In other words, the substance which was one of the predecessors of living matter becomes destructive for the organism under certain conditions. This biochemical paradox deserves to be discussed separately.

Biochemical Effects of Cyanides

As early as the 1860's, it was noticed that venous blood of animals poisoned by cyanides acquires a red, arterial color. Shortly after that the cause of this phenomenon was established. It was found that such venous blood contains almost the same amount of oxygen as arterial blood (up to 17 vol. %). At the same time, the formation of carbon dioxide in the tissues drops sharply. All this gave a reason to believe that cyanides inhibit the ability of the cell to assimilate oxygen. It is quite evident that biological structures which consume oxygen most intensively will be particularly sensitive to such oxygen deficiency. And these are, primarily, the cells of the nervous system, particularly

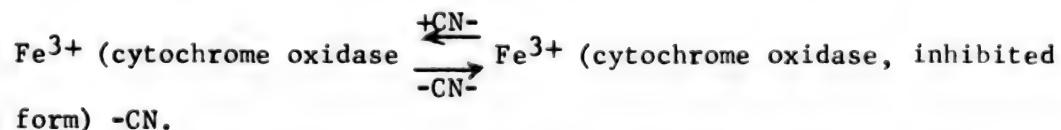
those of the neuroreceptor system. It was found that particularly sensitive to the inhibition of cell respiration were the chemoreceptor cells of the carotid glomeruli, which react to the action of cyanides by acute excitation, which, in turn, leads, as a reflex, to a very strong dyspnea and stenocardia attack. In general, all basic symptoms of acute cyanide poisoning are nothing but the manifestation of an acute oxygen deficiency in the nervous system which, in the final analysis, leads to the development of the convulsive-paralytic syndrome. What is the molecular mechanism of these phenomena?

It is known that biological oxidation (the so-called tissue respiration) is based, on the one hand, on the ability of the biochemically active oxygen to interact with various substances, and on the other, on dehydrogenation reactions with subsequent transfer of the hydrogen from the substrate to the oxygen. The modern conceptions about tissue respiration combine these two parts of the single process into one, whose molecular essence was revealed in connection with studies on the action mechanism of cyanides.

In order to understand in what biological structures the toxic effect of cyanide compounds is realized, let us examine the final stage of oxygen consumption in the cells. This stage includes a group of catalysts, cytochromes, consisting, according to modern conceptions, of five components: b, c, c₁, a and a₃ (it is customary to refer to cytochrome a₃ as cytochrome oxidase). Cytochromes, chiefly, are present in the mitochondria of all cells of aerobic organisms. Cytochromes include iron-containing groups which are close to the heme of hemoglobin in their structure, but, unlike it, their iron atoms change their valency very easily ($\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+}$). It is this property that defines cytochromes as

carriers of electrons in the respiratory system. The successive migration of electrons in the group of iron-containing enzymes ends at the cytochrome oxidase from which the electrons arrive directly to the oxygen. As S. Rouza figuratively described it, "the chain of cytochromes is similar to a team of basketball players passing the ball (electron) from one player to another, inexorably bringing it closer to the basket (oxygen)"⁵. This occurs because the energy level of the electrons in the initial substance is higher than in the end substance, and the movement of the electron through the chain of cytochromes is accompanied by energy release. The activated oxygen (negatively charged ion) interacts with the atoms of the activated hydrogen (protons), and as a result of this there form molecules of water -- one of the main end products of oxidation⁶.

In 1982, O. Warburg showed that the cyanide ion, due to its special chemical affinity to trivalent iron, interacts selectively, although reversibly, with oxidized molecules of cytochrome oxidase:



This blocks up the formation of the reduced cytochrome oxidase, and, consequently, the ability of this enzyme to return electrons to the molecules of oxygen.

As a result of this, the normal level of tissue respiration drops, and oxygen deficiency occurs in the organism, at which time a paradoxical phenomenon is observed: the oxygen content in many cellular structures is high, but this oxygen is chemically inert.

At a low level of oxygen metabolism, the sensitivity of the organism to cyanides decreases sharply. This can be illustrated by citing an interesting fact established at the beginning of this century by a prominent pharmacologist, N. P. Kravkov: during hibernation, hedgehogs can withstand doses of potassium cyanide which are many times higher than lethal doses. It is clear that under such conditions, the need of animals in oxygen at a low body temperature decreases, and, consequently, their resistance to hypoxia increases.

The accumulated experimental material shows that cyanides inhibit also other enzymes whose active centers contain metals with variable valences. Moreover, there is evidence of their inhibiting effect on enzymes catalyzing the biotransformation of a number of vitally important amino acids, such as histidine, tryptophan and tyrosine. However, it should be stressed that the degree of inhibition of the above enzymes is not high, while cytochrome oxidase is inhibited by cyanides in the majority of cells and tissues by 80-90%.

Thus, the specific toxic effect of cyanide compounds is based on their ability of interacting with the transitional metals of enzyme structures whose functions are disturbed in this case.

Cyanides As Radioprotectors

The ability of cyanides to cause oxygen deficiency in the tissues was unexpectedly useful for preventing radiation damages. It is known that ionizing radiation can affect cellular structures both directly (ionization or excitation of biomolecules due to the emission or transition of electrons to a higher energy level), and indirectly. In the second case, the biological effect of radiation is realized through the product of the radiolysis of water. In the presence of oxygen, from water molecules, under the influence of ionizing radiation, there form short-lived, but biochemically active molecules and free radicals which react with the mitochondrial enzymes of tissue respiration.

It has already been clearly established that the organism is less sensitive to irradiation and vice versa under the conditions of hypoxia. Evidently, this is explained by the fact that the course of a number of the primary chemical reactions caused by irradiation and, primarily, the formation of highly active products of radiolysis depend greatly on the presence of oxygen in the medium.

It has been known for more than 30 years that sodium and potassium cyanides administered to animals in maximum tolerance doses directly before irradiation increase their survival rate by 60-85%. It was also found that, with the aid of hydrocyanic acid derivatives, it is possible to increase the protective effect of thiolic radioprotectors: cysteine, glutathione, and others. However, the very high toxicity of the salts of hydrocyanic acid makes it possible to speak only of the theoretical significance of their antiradiation effect. In this connection, experiments which clearly demonstrated the radioprotective

effectiveness of amygdalin when it was administered to animals several hours before irradiation deserve attention. No signs of toxic effects of the preparation were detected in the experiment.

It is clear that the action mechanism of amygdalin is based on its ability to lower the level of oxygen metabolism in radiosensitive tissues and organs (as a result of hydrolysis with the release of hydrocyanic acid). By these means amygdalin protects the enzymes against the damaging effect of the products of the radiolysis of water⁷. A number of authors emphasized also the inhibiting effect of cyanide compounds on the oxydizing effects of free radicals and inhibition of the formation of peroxides by them.

Of course, practical significance of other radioprotectors, primarily that of thiol preparations, is considerably greater than that of amygdalin. However, it can play a definite role in the prevention of radiation complications from roentgenradiotherapy and in weakening the possible effects of sources of ionizing radiation in industry and in laboratories. In this connection, it is necessary also to consider the weakening effect of cyanides on the synthesis of acetylcholine whose amount increases considerably in the blood and tissues after irradiation (as is known, excessive amounts of acetylcholine produce a denaturing effect on protein structures).

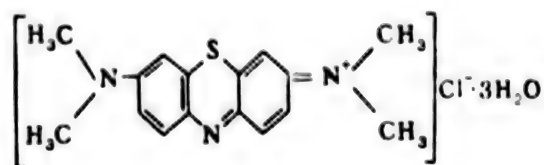
Anticyanides and Mechanisms of Their Action

At the end of last century, biochemists noticed the ability of oxidized hemoglobin, methemoglobin (Mt Hb) to combine rapidly with the cyanide ion and thus protect the respiratory enzymes against the inhibiting effect of cyanide⁸. However, it was only in 1929 that Romanian investigators K. Mladoveanu and P. Georgiu demonstrated the toxicological significance of this fact by saving the life of dog poisoned by a lethal dose of cyanide with the aid of sodium nitrite, a strong methemoglobin producer.

As is known, the change of hemoglobin into methemoglobin is based on the transformation of the bivalent iron of its molecules into trivalent iron. Such a change in the chemical structure makes it impossible for hemoglobin to combine with oxygen. Unlike oxyhemoglobin (HbO_2), in which oxygen is combined unstably with the atoms of bivalent iron, methemoglobin (more precisely, the atoms of trivalent iron) binds negatively charged hydroxyl groups.

Interacting with the cyanide ion, methemoglobin forms a nontoxic complex -- cyanmethemoglobin. However, methemoglobin not only binds the cyanide circulating in the blood, but also removes it from the blocked respiratory enzyme, i.e., produces a reactivating effect against the background of intoxication that has already developed. However, the molecular nature of this process is still unclear in many respects. It is quite evident that methemoglobin does not interact directly with respiratory enzymes. Due to the reversibility of the reaction of their inhibition, CN-ions constantly circulate in the biophase and, evidently, due to their greater chemical affinity with methemoglobin than with cytochrome oxidase, freely diffuse into erythrocytes. It is believed that this shifts the balance in the direction of the formation of free cytochrome oxidase molecules. Consequently, this antidotal effect is based on the competition of methemoglobin and the respiratory enzyme for their binding with the toxic radical.

The known methemoglobin-forming antidotes also include methylene blue (tetramethyltoninon chloride): [sic].



This substance has a high oxidation-reduction potential, which creates equilibrium in the blood between its oxidized and reduced forms, on the one hand, and hemoglobin and methemoglobin, on the other. This fact determines the multidirectional effect of methylene blue on hemoglobin: its large doses (250-300 mgk) stimulate the formation of methemoglobin, and doses 5-6 times smaller, on the contrary, facilitate its reduction to hemoglobin. It has been established also that methylene blue *interferes* in the process of cellular oxidation as a hydrogen acceptor: since in the mechanism of the toxic effect of cyanides an excess of protons inhibits the reactions of biological oxidation in cellular structures, their binding will, on the contrary, stimulate these reactions. However, it is practically impossible to separate this effect of methylene blue from the effect of methemoglobin-*formed* during cyanide intoxication.

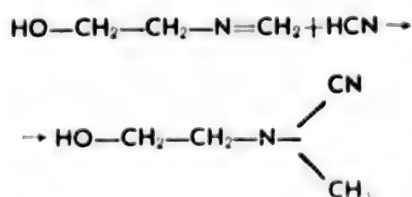
By and large methemoglobin-forming preparations, particularly nitrites, are toxic because they deprive hemoglobin of its main property: its capability to carry oxygen from the lungs to the tissues. In a sense, it is the case when a poison acts as an antidote: an artificially caused oxygen deficiency in the blood counterbalances histotoxic hypoxia. Consequently, the formation of methemoglobin during cyanide intoxication must not exceed a certain limit (25-30% of the total mass of hemoglobin). Since the cyanmethemoglobin-formation reaction is reversible, the cyanide-ion separated during dissociation can cause re-intoxication. In this connection, toxicologists recommend to use preparations which would stably hold the poison and would speed up its removal from the organism. They include: glucose, sodium thiosulfate, cobalt compounds and some other substances. The molecular action mechanisms of glucose and sodium thiosulfate are identical to the mechanisms of the detoxication of cyanides in the liver cells, i.e., they amount to formation of cyanhydrins and thiocyanogen compounds⁹. However, glucose and thiosulfate act considerably slower than nitrites. They do not reduce the inhibited respiratory enzyme. It is recommended to administer them together with methemoglobin-forming agents or prior to expected intoxication. Many years of practice indicate that it is most effective to administer gradually sodium nitrite (or amyl nitrite) and thiosulfate to the poisoned person. This antidotal combination protects against 10-20 lethal doses of cyanide.

As was shown in our laboratory, when animals are poisoned by lethal doses of sodium cyanide, a good protective effect is produced by heparin, a mucopolysaccharide which is used widely in clinics as an anticoagulant¹⁰.

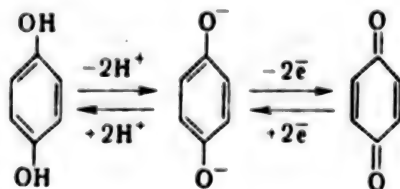
As for cobalt compounds, their chemical affinity with cyanides, which was known since the end of last century, started being used only since the appearance of low-toxicity cobalt complexes. Organic compounds of cobalt which include atoms of sulfur are also of definite interest as anticyanides.

Vitamin B^a₁₂ (hydroxocobalamine), in whose molecule the hydroxyl group is added to the cobalt atom, was also found to be an anticyanide. Its detoxication effect consists in the substitution of hydroxyl with CN-group with subsequent formation of cyanocobalamin (vitamin B₁₂).

Experimental toxicology has a few more anticyanide preparations. For example, it was established¹¹ that animals can be saved from 1.5-2 lethal doses of cyanide if they are administered β-Hydroxyethylmethylene amine which forms a nontoxic complex with the poison:



Some acceptors and donors of electrons and protons could become promising anticyanides. Such substances include hydroquinone, which occurs simultaneously in three forms in an aqueous medium -- neutral, oxidized and reduced:



The ability of hydroquinone to accept electrons was used successfully in experimental cyanide intoxication¹². It is believed that, under the conditions of tissue hypoxia, hydroquinone "unloads" the respiratory enzymes from the excess of electrons and, moreover, activates the dehydratase section of cellular oxidation, which is resistant to cyanides.

Thus, the store of antidotal therapeutic means for cyanide intoxication is sufficiently great: however, the search for new substances of such type of action is continuing.

And so, cyanide compounds are characterized by various chemical properties and a very selective effect on the organism. On the one hand, they are considered to be among the main predecessors of biological molecules and, consequently, it is impossible to imagine the origination of living matter without their participation. On the other hand, their extraordinary chemical activity and their ability in negligibly small doses to inhibit and block the functions of vitally important biological structures make them highly toxic substances. At the same

time, this property of cyanides can be useful when it is necessary to weaken the intensity of oxygen consumption by organs and tissues, for example for the purpose of preventing the effects of ionizing radiation. It can be seen clearly on the example of cyanide compounds how the understanding of the ways of the transformation of a heterologous substance in the organism and its molecular mechanism of biochemical activity makes it possible to develop effective specific means for controlling intoxication.

Great interest in cyanides of toxicologists, chemists, biochemists and other specialists indicates that the use of these substances in various spheres of activity is promising, including experimental studies.

Footnotes

1. Cyanides(cyanide compounds) is a term used in chemistry to denote, according to the radical-functional system, substances containing a CN group in their molecules. There is another name for them: nitriles (according to the substitution nomenclature), which are, essentially, understood to denote organic derivatives of prussic acid.
2. Prussic acid $\text{H}-\text{C}\equiv\text{N}$ [synonyms: hydrogen cyanide, nitrile of formic acid) is a light volatile liquid having a characteristic odor of bitter almond.
3. Franke, Z. "Khimiya otravlyayushchikh veshchestv" [Chemistry of Poisoning Substances], translated from German, edited by I. L. Knunyants and R. N. Sterlin, Moscow, 1973, Vol 1 p 218.
4. Although lately the share of hydrocyanic acid in the production of acrylonitrile has somewhat decreased (due to the appearance of a new method of its synthesis), its consumption in the production of acetonecyanohydrin and methacrylic acid ester has increased. A considerable amount of hydrocyanic acid is reprocessed in amino acids and detergents.
5. Rouz, S. "Khimiya zhizni" [Chemistry of Life], Moscow, 1969, p 139.
6. It is appropriate to mention here that, through the functioning of the cytochrome group of enzymes, not only the processes of oxygen consumption in cellular structures are realized, but also the detoxication of heterologous substances in them is ensured by a special monooxygenase system with a mixed function (see: Kovalev, I. Ye., and Malenkov, A. G. "Stream of Heterologous Substances: Their Influence on Humanity", PRIRODA, 1980, No 9, p 90).
7. Rogozkin, V. D., Belousov, B. P. and Yevseyeva, N. K. "Radiozashchitnoye deystviye tsianistykh soyedineniy" [Radioprotective Effect of Cyanide Compounds], Moscow, 1963.
8. It has been proven that, under normal conditions, human and animal erythrocytes contain from 1 to 2% methemoglobin. Its detoxication role was first noticed by N. N. Savitskiy in 1916. Specifically, he showed that physiological methemoglobin is sufficient for detoxifying one third of the lethal dose of cyanide. Evidently, the protective effect of methemoglobin in relation to endogenous cyanides also cannot be excluded.

MICROBIOLOGICAL SYNTHESIS OF FODDER PROTEIN FROM NATURAL GAS

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 20 Dec 83 p 1

[Article by I. Mordvintsev, correspondent, Svetlyy Yar, Volgograd Oblast]

[Text] The Svetlyy Yar plant for producing protein vitamin concentrates has used an apparatus--which has no analogs either in our country or abroad--to prepare the first kilograms of product. For the first time, the apparatus will begin production of Gaprin, a fodder protein made from natural gas.

I am going to the plant. Construction, lost in the middle of the working enterprise, has considerably spoiled the external appearance of the plant: piles of not-cleared-away soil, now and then wandering cars. But it cannot be helped: the future is being born here and not only of this plant but of the whole industry. The apparatus, on the face of it, is nothing unusual: processing tower, one of these you see at every chemical enterprise, with an infinite mane of pipes hurrying toward it. Nevertheless, the process taking place here is just inconceivable: natural gas at the input, and a protein concentrate at the output--a valuable product for fattening cattle. In addition, every ton of such a concentrate saves about seven tons of grain.

Says R. Kartush, the head of VNIIsintezbelok institute: "It started when we discovered, in soil around one of the oil refining plants, strains of bacteria capable of synthesizing protein in an environment of natural gas, such as ordinary methane." Does that mean that the apparatus at the plant in Svetlyy Yar was designed from scratch? Not at all. For almost ten years the new method was being developed using a small experimental apparatus in Nartkala village, Kabardino-Balkar ASSR. Several different technological alternatives have been tested. Several dozen tons of product have been manufactured, which then underwent thorough medical and biological testing, and, at present, is released by Minselkhoz SSSR [USSR Ministry of Agriculture] and Minzdrav SSSR [The USSR Ministry of Health] for utilization.

Gaprin obtained from methane contains up to 75 percent of crude protein and, also, other valuable substances and many vitamins. In addition, industrial production of biomash from gas will be noticeably cheaper.

9. For more detail see: Oksengendler, G. I. "Biotransformation of Heterologous Substances", PRIRODA, 1980, No 3, p 18.

10. Oksengendler, G. I. and Nazarov, G. F. "On the Effect of Heparin on the Course of Cyanide and Nitrite Intoxication in an Experiment", VNIIMI [All-Union Scientific Research Institute of Medical and Medicotechnical Information] of the USSR Ministry of Health, No. D-1831, "MRZh", 1978, Section XII, No 10, Publication 2642.

11. Rozenberg, V. N. "On the Antidotal Properties of β -hydroxyethylmethylenamine in Cyanide Poisoning", FARMAKOLOGIYA I TOKSIKOLOGIYA, 1967, No 1, p 99.

12. Vinogradov, V. M. Pastushenkov, L. V. and Frolov, S. F. "The Use of Electron Acceptors for the Prevention and Treatment of Oxygen Deficiency", in the Collection "Izyskaniye i farmakologicheskoye issledovaniye veshchestv, povyshayushchikh ustoychivost' organizma k chrezvychaynym vozdeystviyam" [Investigation and Pharmacological Tests of Substances Increasing the Resistance of the Organism to Extreme Effects], Leningrad, 1968, p 111.

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CSO: 1841/112

Adds A. Grigorian, chief of the laboratory of the VNIIsintezbelok institute:
"The new apparatus is designed in such a way that, in principle, it will allow work not only with methane but with use of methyl alcohol as well."

And what perspectives are being opened up by the new biotechnology? This is how this question was answered by the Deputy Chief of USSR Glavmikrobioprom, M. Sobolev:

"Our immediate goal is to bring the first fermenter into a minimal operating mode with a yield of, if only, two tons a day. The next step is the intensification of the process. Then, we begin building a fermenter with a considerably higher working volume. Such a unit will serve as a prototype for future gigantic plants". We have no doubts that these plans will succeed.

12603

CSO: 1841/93

PLANT GOES ONSTREAM

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 8 Jan 84 p 1

[Article by L. Aleynik]

[Text] The Mozyr Plant of Fodder Yeasts is growing and growing; the first of its line, which is going onstream, has a calculated output of 30,000 tons of production a year, and in the future it will begin to produce 10-fold more. The addition of yeast into rations of animals and birds guarantees a significant weight gain. And the inexpensive raw material for industrial biosynthesis--purified paraffins from the neighboring oil refining plant--places the plant in the category of highly effective, most important enterprises for the realization of the Food Program.

At the republic main komsomol construction project, envoys from Czechoslovakia, Hungary and the GDR have worked alongside Soviet builders and installers--it had become a site of friendship. Collectives of the general contracting trust "Mozyrneftekhimstroy" and numerous subdivisions of the USSR Ministry of Installation and Special Construction widely spread socialist competition of coworkers on the principle of the "work race" and actively introduced the brigade contract.

Installers of the "Neftezavodmontazh" have especially distinguished themselves: in short amounts of time, they set up more than 1000 units of basic technological equipment, laid out 125 kilometers of technological pipe-lines of different diameters and assembled more than 5000 tons of steel structures.

Contract brigades of M. Puzikov, G. Baglay, T. Dergachev, R. Rychkov, D. Tarasenko and others became leaders of the competition.

12473

CSO: 1841/137

UDC [661.721.4.004.14:636.087.7].003

EFFECTIVENESS OF METHANOL USE AS STARTING MATERIAL IN PRODUCTION OF MICROBIAL FEED PROTEIN

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 12, Dec 83 pp 719-720

SGADLEV, B. F. and KAUFMAN, G. M.

[Abstract] There exists a 15-17% deficit in feed protein for agricultural animals and poultry in the USSR. The existing factories producing microbial feed proteins are not and will not be able to satisfy the need of the country up to at least 1990. The authors reviewed the efforts abroad in using methanol as the starting material for microbial feed protein. The remainder of the paper was devoted to economical analysis aimed at showing that development of methanol-based microbial production of feed protein will supply agriculture with the necessary high quality food additive. References 8: 1 Russian, 7 Western.

[120-7813]

UDC 577.152.31:612.822

RELEASE OF ^{14}C ACETYLCHOLINE FROM SYNAPTOSOMES UNDER EFFECT OF PRESYNAPTIC NEUROTOXINS FROM SNAKE AND BEE VENOMS--PHOSPHOLIPASES A_2

Moscow BIOKHIMIYA in Russian Vol 48, No 11, Nov 83
(manuscript received 10 Jan 83) pp 1799-1803

TERLETSKAYA, Ya. T., KOCHERGA, V. I., KOZULINA, Ye. P., SYROVATSKAYA, L. P. and MIROSHNIKOV, A. I., Institute of Biochemistry imeni A. V. Palladin, UkSSR Academy of Sciences, Kiev; Institute of Bioorganic Chemistry imeni M. M. Shemyakin, USSR Academy of Sciences, Moscow

[Abstract] Study of the effect of phospholipases A_2 from bee and snake venoms on uptake of ^{14}C choline and liberation of ^{14}C acetylcholine by synaptosomes of the rat brain striate body showed that phospholipases A_2 from snake and bee venoms, liberate acetylcholine synthesized from extracellular choline in synaptosomes on one hand, and, block reuptake of choline by the nerve endings, on the other. It is assumed that the blocking of synaptic transmission observed in neuromuscular preparations is based on these processes. Figures 3; references 12: 4 Russian, 8 Western.

[91-2791]

BIOCHEMICAL CRITERIA OF MAMMALIAN CELL SENSITIVITY TO GLUCOCORTICOIDS

Moscow BIOKHIMIYA in Russian Vol 48, No 11, Nov 83
(manuscript received 4 Feb 83) pp 1849-1854

POLOTSKAYA, A. V., ADLER, V. V., KRASIL'NIKOV, N. A., DMITRIYEVA, L. V. and SHAPOT, V. S., Scientific Research Institute of Cancerogenesis of the All-Union Oncological Scientific Center, USSR Academy of Medical Sciences, Moscow

[Abstract] Study of resistance to glucocorticoids of Morris hematoma strain 8894 cells which did not produce induction of tyrosine aminotransferase synthesis by the hormone is described and discussed. Morris hematoma strain 7777 cells were used as a sensitive cell population according to the criterion of induction of tyrosine aminotransferase synthesis. It was concluded that the resistance of this or that cell population to glucocorticoids cannot be determined by analyzing the synthesis intensity of one or even several proteins; glucocorticoids regulate the activity of a whole block of genes; genes in different cell strains involved in the regulation may differ and a protein marker such as tyrosine aminotransferase may not be involved in hormonal control; further regulation by glucocorticoids may involve not only activated genes but also genes the expression of which is suppressed. It was finally concluded that the resistance of any cell population to glucocorticoids requires the use of a great many experimental approaches if there is no disturbance in the receptor apparatus. Figures 3; references 9: 1 Russian, 8 Western.
[91-2791]

CATALYSIS

PHOTOSYNTHETIC PROCESS ADAPTED FROM GREEN LEAVES

Riga SOVETSKAYA LATVIYA in Russian 12 Oct 83 p 2

[Article by M. Kuryachaya]

[Text] An artificial model of photosynthesis has been created in our country. This achievement of scientists opens prospects outside the boundaries of science: the use of artificial photosynthesis can bring innovations to energetics, agriculture and other sectors. APN [Novosti Press Agency] Correspondent M. Kuryachaya reports from the laboratory where artificial photosynthesis was realized for the first time in the world.

"The chief will arrive in 15 minutes. It is worth waiting for him," a young man in a lab coat told me, pointing to a chair by the window. The chief is Aleksandr Yevgen'yevich Shilov, corresponding member of the USSR Academy of Sciences. I have arrived at the laboratory of catalysts, headed by him, of the Moscow Institute of Chemical Physics.

"Would you like to see a trick?" asked the young man. He got a flask, which resembled the shape of a maple leaf. Some kind of yellow solution was poured into it.

"Put it on the window-sill," said the lab assistant and he left. The "leaf" came to life by the window. The tiny bubbles of gas began to gurgle, and before my eyes it changed from a fall leaf into a spring leaf by itself. Finally, under the rays of the sun it became completely green.

"Are you getting acquainted with our hydrogen model of photosynthesis?" I heard. Absorbed in the changes occurring in the flask, I didn't notice that A. Ye. Shilov had entered the laboratory.

An Alluring Task

"From your botany course in school," said the scientist, "you know that under the effect of solar energy, a reaction of photosynthesis occurs in real leaves and a gas is released into the atmosphere..."

"Oxygen," I recalled.

"In this case, hydrogen is released into the light. Hydrogen, like oxygen, is a product of the photosynthesis reaction which occurs in a green leaf. But plants do not give off hydrogen into the atmosphere, as occurs in our model, yet they do use it for their purposes."

"And what is the point of the photosynthesis reaction?"

"To convert the light energy of the sun into chemical energy. This is precisely what occurs in this model. The light "launches" a series of chemical reactions, as a result of which hydrogen is produced. As early as 1975, we began to work on developing scientific bases for using solar energy by means of artificial photosynthesis outside of an organism..."

Imagine! Everyday, every hour, every moment, streams of solar energy are traveling from space to Earth. Animate nature is assimilating an insignificant part of it, but there is enough of it so that life develops on Earth and, with photosynthesis, chemical energy protects all organisms. To get to know and be able to use the photosynthesis process means to solve energetic, food and many other problems in the future.

To Learn. But How?

When starting this task, it was clear to A. Ye. Shilov that there is no point in copying nature. The interaction of processes occurring in a living cell are too complex and perfected to reproduce them in a laboratory. And even having overcome this complication, man, at best, will receive only what the surrounding world will give to him in plenty. So it was necessary to study from nature in order to understand which principles lie at the basis of the functioning of green leaves. And having learned, to use those principles.

It is known that plants cannot live without water and sun. It is also known that in the photosynthesis process in green leaves, carbonic acid and water are absorbed under the influence of sunshine. Chemists have been studying the complex mechanism of photosynthesis for more than 200 years, attempting to find just what occurs with water and what its path in cells is before it is broken down into hydrogen and oxygen.

Put a glass of water in the sun. A sunbeam does not evoke any kind of chemical reactions in it. But they occur in tiny cells... During electrolysis, the production of hydrogen and oxygen from water requires much electrical energy. Yet energy expenditures in cells are minimal...Why? Processes occurring in plants are given amazing facility and speed by chlorophyll, to which the green leaf owes its color, enzymes and other complex biological compounds.

Thus, the green leaf prompted them to search for compounds which function like chlorophyll and enzymes.

"He who seeks, must roam," said Goethe. As every genuine search, the search for a chemical model which decomposes water into its components, has in its

service record both failures and incorrect conclusions. But experiment followed experiment, and the researchers found what they wanted. They succeeded in substituting synthetic dyes for chlorophyll, and for other complex biological compounds--artificial analogs, also taken from inanimate nature. And so a water solution was found: a traditional catalyst--platinum. The very first ray of light causes a few chemical conversions in the solution. The inanimate functions like the animate. Hydrogen was released from the water without the assistance of chlorophyll and enzymes. This was accomplished for the first time in the world by the Institute of Chemical Physics.

Rival of Solar Devices

In the opinion of specialists, artificial photosynthesis opens new horizons for solar energy. There are two fundamental shortcomings in modern solar devices. In the first place, there is the irregularity in the operation of the solar devices (in cloudy weather the device does not work), and in the second place, the imperfection of batteries hinders accumulation of solar energy. A hydrogen device, operating on the principle of photosynthesis, would make it possible to use the sun's energy throughout the entire day. It would not prove difficult to collect energy received by such a device: hydrogen is convenient to handle, it can be stored in any quantities, transported through pipes, and spent at any time. When burning, hydrogen releases three times more heat than gasoline, but in contrast to it, hydrogen does not pollute the air at all: the product of its burning is water.

Of course it is still early to be speaking of such devices and about industrial use of photosynthesis. As yet, the problem has been solved only in principle: staff personnel of the laboratory have proven that it is possible to produce fuel with photosynthesis. For this they did not use animate nature to help them (in contrast to creators of experimental devices, which use chlorophyll and enzymes to produce hydrogen). Efforts to increase efficacy of "non-natural"--using the language of specialists--photosynthesis are still forthcoming.

One More Model

But what is the future of the second component of a water molecule--oxygen? What happens to it in the green leaf? The answer to this question will help in recognizing laws which govern plant growth and their productivity. Along with the hydrogen model in the laboratory, an oxygen model was also created. The lab assistant did some "concocting" over another flask, and, when I put it in the light, tiny bubbles also gurgled.

"In the solution," explained Aleksandr Yevgen'yevich Shilov, "is a manganese compound. It acts as a catalyst, making it possible to draw out the oxygen. Now, when the model has been created, it even seems strange that not one of the numerous researchers of photosynthesis could have used a circumstance which is well known to specialists: it amounts to excluding manganese from the photosynthesis process, as the plant stops discharging oxygen. It is as if the green leaf prompted us: manganese serves as the catalyst. We used this prompt and finally found a non-natural manganese compound which makes it possible to create an oxygen model. It helps us to understand better how plants decompose water."

"So, until the end it is still not clear?"

"What do you mean? The green leaf will still teach a great deal."

"But what is it teaching now?"

"How to unite a hydrogen and oxygen model into one whole. After all, a single model, so to say, functions in a leaf. When we create it, new discoveries will be possible."

12473

CSO: 1841/137

POSSIBILITY OF REACTIVATING POISONED CATALYSTS DISCUSSED

Moscow KHIMIYA I ZHIZN' in Russian No 1, Jan 84 p 37

[Article by V. Zyablov: "Latest News: A Catalyst Yields to Treatment"]

[Text] A reaction has been found as a result of which complexes of palladium poisoned by sulfur compounds become active catalysts again.

The most reliable and effective processes of chemical technology are catalytic. The most delicate and finest laboratory syntheses are also such. However, catalysts, just as everything fine and delicate, are characterized by their vulnerability: the slightest admixture of some "hostile" substances completely kills their activity and poisons them (this term, which seems to be inapplicable to inanimate objects, has long since become generally accepted among chemists and is written without any quotation marks). Sulfur compounds are among the most harmful substances. Binding stably with atoms of transition metals, which are, as a rule, active centers of catalysts, mercaptans, sulfides or disulfides block them and make it impossible for all other molecules to get to the active point. Due to this, it is necessary to purify the raw material in all catalytic processes very thoroughly, which sharply increases the cost of production; for the same reason it is difficult to use some oil deposits which contain large amounts of sulfur...

It was believed that there was no way out of this situation. However, studies conducted in 1983 (A. S. Berenblyum, S. L. Mund, L. G. Danilova, T. P. Goranskaya, A. S. Malinovskiy, and I. I. Moiseyev; ISVESTIYA AN SSSR, Chemical Series, 1983, No 8, p 1926) showed that poisoned catalysts are not hopeless: it is possible to find a "medicine" for them.

The following experiments were carried out: catalysts, soluble complexes of palladium belonging to the so-called cluster class, were thoroughly poisoned with diphenyl sulfide. In order to ensure the loss of activity, the "poison" was introduced in a five-fold excessive dose, after which the activity of the solution in the process of the hydrogenation of olefins was reduced to zero. And only after this the object of hydrogenation was changed by introducing derivatives of acetylene and butadiene into the medium. Something unexpected happened when hydrogen was fed under pressure: the gas which was not absorbed and had no effect on the solution before suddenly started being consumed. The catalyst acted sluggishly at first, but after about ten minutes it started acting as if there had been no poisoning.

The explanation of the result proposed by the authors is very simple: acetylenes and dienes, evidently, have the ability to intrude into the bonds among the palladium and sulfur atoms, removing the blockage from the active center in this way. Preliminary experiments with the use of acetylene seem to confirm this hypothesis: sulfides which, by all appearances, are of "acetylene" origin have been isolated, however, their structure still has to be defined more accurately.

These conclusions would be premature (this is a preliminary report), however, achievements of this kind, as a rule, always leave their trace.

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CSO: 1841/121

UDC 547.313 + 542.941.7

INVESTIGATION OF FORMATION PROCESS OF COMPLEX PALLADIUM CATALYSTS FOR
SELECTIVE HYDROGENATION OF CONJUGATED DIENES TO OLEFINES

Moscow KINETIKA I KATALIZ in Russian Vol 24, No 6, Nov-Dec 83
(manuscript received 8 Jul 82) pp 1385-1390

SHUYKINA, L. P., BONDARENKO, G. N., CHERKASHIN, G. M., PARENAGO, O. P. and
FROLOV, V. M., Institute of Petrochemical Synthesis imeni A. V. Topchiyev,
USSR Academy of Sciences, Moscow

[Abstract] The process of the formation of palladium catalysts was investigated by kinetic and IR-spectral methods. The catalysts were prepared by a two-stage method. First anhydrous palladium chloride was reacted with heteroatomic ligand (amines or sulfides) in absolute toluene at 60-70°C in dry argon for 30-40 hrs yielding yellow-orange complexes. In the second phase, these complexes were treated with diisobutylaluminum hydride at 20°C yielding a dark brown product. Introduction of water during the first stage yielded an active catalyst immediately after reaction with diisobutylaluminum hydride; in absence of water the product was not active as a catalyst until molecular oxygen was added to the system. To obtain optimal catalytic activity an equimolar quantity of Pd and O₂ should be used. Analysis of kinetic and IR data indicated that appearance of catalytic properties in the palladium complexes studied was related to the presence of acidoligands in the starting complexes of palladium chloride with primary amines or sulfides. Figures 4; references 7: 4 Russian (2 by Western authors), 3 Western (1 by Russian authors).
[135-7813]

UDC 554.172

METAL ION POISONING OF PLATINUM CATALYST IN SYNTHESIS OF HYDROXYLAMINESULFATE

Moscow KINETIKA I KATALIZ in Russian Vol 24, No 6, Nov-Dec 83
(manuscript received 27 May 82) pp 1391-1395

APEL'BAUM, A. L., LOPATIN, V. L., KUL'KOVA, N. V. and TEMKIN, M. I.,
Scientific Research Physical-Chemical Institute imeni L. Ya. Karpov, Moscow

[Abstract] Synthesis of hydroxylaminesulfate is carried out over platinum catalyst deposited on porous electrographite. During the reaction, iron,

nickel, chromium, molybdenum and copper may be liberated and dissolved in the solution, poisoning the catalyst and requiring its regeneration. Experimental results were reported of study of the platinum catalyst poisoning. Analysis of the data showed that the effect of Cr^{3+} , MoO_2^+ and Cu^{2+} ions on hydrogenation of nitrogen oxides was linearly related to the positivity of electrode potentials of corresponding metals; Cr^{3+} ($E^\circ = -0.744$ V) ions do not change the rate of the formation of hydroxylamine and ammonia and they increase formation of N_2O only at high concentrations; MoO_2^+ ($E^\circ = -0.08$ V) ions retard formation of hydroxylamine but increase formation of ammonia and N_2O , and, the Cu^{2+} ($E^\circ = 0.344$ V) ions retard formation of hydroxylamine and ammonia but sharply increase formation of NO_2 . References 7: 5 Russian, 2 Western. [135-7813]

UDC 541.128

DEUTERIUM ISOTOPE EXCHANGE BETWEEN HYDROCARBONS OVER NICKEL-COPPER SUPPORTED CATALYSTS

Moscow KINETIKA I KATALIZ in Russian Vol 24, No 6, Nov-Dec 83
(manuscript received 25 Feb 83) pp 1423-1427

KHOTULEVA, M. V., GUDKOV, B. S., PIMENOV, V. G., SLINKIN, A. A. and KIPERMAN, S. L., Institute of Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow

[Abstract] Studies of the properties of polymetallic supported systems concern some of the most important problems in the development of the theory of catalysis over metals and alloys. Many questions concerning the relationship between the volume and surface composition and interaction between the alloy components remain unsolved because of different properties of the catalysts studied. In the present paper, results were reported of the study of catalytic properties of nickel-copper systems on silica gel support in the reaction of deuterium exchange between n-hexane and cyclohexane and the relationship between surface composition and the copper content within the sample. It was shown that surface composition of these catalysts did not differ much from that of the volume composition. Recalculated to one surface atom of nickel, the specific activity in the deuterium exchange of hydrocarbons decreases gradually with increased content of copper on the surface of the catalyst. The ligand and cluster effects on this behavior were discussed without reaching a positive conclusion in favor of one of them. Figures 2; references 10: 4 Russian, 6 Western. [135-7813]

HYDROGENATION OF CARBON MONOXIDE ON DEPOSITED COPPER-CONTAINING CATALYSTS

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA
TEKHNOLOGIYA in Russian Vol 26, No 12, Dec 83 (manuscript received 17 Dec 81)
pp 1514-1516

MOROZOV, L. N., KOSTROV, V. V. and BESSONOV, V. Ye., Department of Technology
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[Abstract] Study of catalytic properties of deposited model copper-containing catalysts in the process of hydrogenating CO at atmospheric pressure is described and discussed. During CO hydrogenation, methanol, water and carbon dioxide were found on the contacts studied by a chromatographic method. Product yield as a function of the temperature of performing the process is shown for $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ and $\text{ZnO}/\gamma\text{-Al}_2\text{O}_3$. The quantity of methanol formed as a function of reaction temperature reached a peak at 120 to 140°C for all of the catalysts studied. This may be due to thermodynamic limitations or to side reactions. A possible mechanism of CO hydrogenation is described; it includes reactions of vapor conversion of CO, methanol synthesis and formation of paraffin hydrocarbons. Figure 1; references 2 Russian.
[131-2791]

UDC 541.128

RANEY NICKEL CATALYSTS IN CONTINUOUS HYDROGENATION OF BENZENE BY ISOPROPANOL

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA
TEKHNOLOGIYA in Russian Vol 26, No 9, Sep 83 (manuscript received 25 Dec 81)
pp 1045-1047

ZHANABAYEV, B. Zh., ZANOZINA, P. P., UTEL'BAYEV, B. T. and KAMYSBAYEVA, M. M.,
Problems Laboratory, Kazakh Institute of Chemical Technology

[Abstract] Benzene hydrogenation to cyclohexane in a coupled dehydrogenation-hydrogenation catalyzed by activated Raney nickel catalysts doped with Ti, Cr, Zr, Nb, Mo or W was studied to determine the optimum conditions and catalyst. Using a benzene: isopropanol, volume ratio of 1:30, to prevent polymerization of the unsaturated aromatic compound on the nickel surface, conversion of benzene to cyclohexane occurred with 100% efficiency at 80°C and atmospheric pressure with Ni+0.5% Zr and Ni+10.0% Mo catalysts. The calculated apparent energy of activation for this type of hydrogenation was calculated at 34.8 kJ/mole. Figures 3; references 3: 2 Russian, 1 Western.
[130-12172]

REDUCTION KINETICS OF INDIGOCARMIN BY RONGALITE CATALYZED BY COBALT DIOXIMINES WITH DIFFERENT AXIAL AND EQUATORIAL LIGANDS

Ivanovo IZVESTIYA VYSSHIKH UCHEBNIKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA in Russian Vol 26, No 9, Sep 83 (manuscript received 3 Jul 81) pp 1092-1095

TERSKAYA, I. N., SELIFONTOVA, G. Yu. and BUDANOV, V. V., Chair of Physical Chemistry, Ivanovo Institute of Chemical Technology

[Abstract] The catalytic mechanism of action of dioximines in promoting the reduction of indigocarmine by Rongalite was studied through an analysis of the reaction kinetics, using the following cobalt dioximines: $[\text{Co}(\text{SO}_3)_2(\text{MH})_2] \cdot \text{H}_2\text{O}$; $(\text{NH}_4)_3[\text{Co}(\text{SO}_3)_2(\text{Nioxim})_2] \cdot 7\text{H}_2\text{O}$; and $[\text{CoCl}(\text{DH})_2] \cdot \text{H}_2\text{O}$, where MH = methyl glyoxime, Nioxim = cyclohexanedionedioxime, and DH = dimethyl glyoxime. The rate of reduction was determined with respect to indigocarmine concentration, Rongalite concentration, catalyst concentration, acidity (pH 3-11), formaldehyde concentration, and KCl and K_2SO_4 (axial ligands) and DH, MH and Nioxim additives (equatorial ligands). The rate of the reaction was found to be independent of the dye concentration, but directly proportional to the concentration of a given catalyst. Formaldehyde was found to inhibit the reaction through binding to the active products of Rongalite decomposition. These facts, in conjunction with data on the ligand effects, suggest that the catalytic action of cobalt dioximines rests on complex formation with Rongalite, which in turn leads to accelerated dissociation of the reducing agent. Figures 4; references 6 (Russian). [130-12172]

UDC 66.095.253.7.001;661.7:547.535.1

EFFECT OF IMPURITIES ON CATALYTIC PROPERTIES OF A COMPLEX IN ALKYLATION OF BENZENE WITH PROPYLENE

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 12, Dec 83 pp 718-719

YEPIFANOVA, A. G., MICHURINA, S. A., DAVYDOV, I. M., SARKISOVA, I. A. and MALYUTIN, S. A.

[Abstract] The goal of this study was to analyze the effect of hydrogen sulfide, thiophene and water present in the starting benzene on the alkylation process of C_6H_6 with propylene. As one criterion of the effect of impurity, the ratio of polyalkylbenzene to isopropyl benzene (PAB/IPB) obtained in the reaction mixture was determined. This ratio is an objective indicator of the concurrently proceeding, alkylation and dealkylation reactions. The results have shown that catalytic activity is diminished in presence of hydrogen sulfide and thiophene; the yield of IPB is decreased in their presence. The

effect of thiophene is stronger than that of H_2S ; it is manifested immediately at the beginning of the reaction but their mechanisms are different. In presence of H_2S , an inactive form of $AlCl_3$ is formed which is soluble in the reaction mixture and can be removed from the reaction. In presence of thiophene lower activity is due to tarring of the catalyst. Figures 2; references 6 (Russian).
[120-7813]

UDC 661.53.094.373

DETERMINATION OF IGNITION CONDITIONS FOR OXIDE CATALYST USED IN OXIDATION OF AMMONIA

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 12, Dec 83 pp 751-752

KARAVAYEV, M. M., GUBA, N. B., NAKAZNAYA, I. V. and SHIGANOVA, N. K.

[Abstract] Experimental results were reported of the study of the ignition process of a non-platinum catalyst NK-K5 under laboratory conditions. Optimal conditions were determined at which ammonia escape would not occur or at least would be minimal. It was shown that ignition of oxide catalysts can be carried out in time corresponding to the ignition of platinum catalysts using a burner. When the process is carried out at relatively low linear gas velocity, and the content of ammonia in the ammonium mixture not exceeding 8%, the concentration of ammonium nitrate in nitrogenous gases would be lower than in case of the use of platinum catalysts. Figures 4; references 5 (Russian).
[120-7813]

UDC 665.644.4

EFFICIENCY OF SERIES KR POLYMETALLIC CATALYSTS IN REFORMING

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 1, Jan 84 pp 12-14

SHAPIRO, R. N., ZHARKOV, B. B. and LASTOVKIN, G. A., All-Union Scientific Research Institute of Petrochemistry

[Abstract] A brief review is presented of the effectiveness and advantages of polymetallic reforming catalysts in use in the USSR. Currently, the most extensively used catalyst is designated KR-104, and it is anticipated that the immediate future will witness an increasing use of aluminum oxide-based KR-108 and KR-110 catalysts. In addition to markedly improving the octane number by four or more points, the polymetallic catalysts offer the advantage of low cost, greater stability, high selectivity and long service times between regeneration, they decrease the energy and pressure requirements for reforming.
[133-12172]

COAL GASIFICATION

UDC 662.741.3.022:622.765.06

ORGANOSILICON REAGENTS IN COAL FLOTATION

Moscow KOKS I KHIMIYA in Russian No 1, Jan 84 pp 11-14

PETUKHOV, V. N., Magnitogorsk Mining and Metallurgical Institute

[Abstract] A variety of organosilicon compounds was tested for effectiveness as reagents in coal flotation for comparison with commonly used acetals and esters. The organosilicon compounds were found more effective in promoting flotation than standard reagents used for that purpose. The greater efficiency of the organosilicon compounds was attributed to both reactivity with functional groups on the coal surface (as indicated by shifts on IR spectra and the appearance of new bands) and the subsequent orientation of the hydrocarbon tail into the aqueous environment. Replacement of the oxygen atom by a nitrogen atom in the organosilicons reduced their effectiveness and selectivity. Figures 2; references 5 (Russian).
[144-12172]

UDC 668.78:002.6(477)

PRODUCTION OF ELECTRODE PITCH AT UKRAINIAN COAL CHEMISTRY PLANTS

Moscow KOKS I KHIMIYA in Russian No 1, Jan 84 pp 34-37

PITYULIN, I. N., ZAYCHENKO, V. M. and SHUSTIKOV, V. I., Ukrainian Chemical Institute; STETSENKO, Ye. Ya., and SURYADNYI, V. I., All-Union Coke Chemistry Station

[Abstract] An analysis is made of the current status of electrode pitch production in the Ukraine at the various coal chemistry plants. At the present time five categories of electrode pitch are produced on a large scale, amounting to a total productive capacity of approximately 800,000 tons per year. In recent years, however, the quality of electrode pitch produced at the Ukrainian plants has deteriorated for several reasons. One factor responsible for this phenomenon is the coking of inferior quality coal imported from the Eastern and Northern regions of the USSR; another is inadequate or inappropriate maintenance of the coking furnaces resulting in the production of electrode pitch with unacceptably high α_1 fractions. Significant

improvements in the coking techniques and plant maintenance will and have resulted in improved products. It can be expected that a more serious and responsible approach to this problem in the 12th Five-Year Plan will bring further success. References 3 (Russian).
[144-12172]

UDC 539.216.2:621.794.61

ELECTROCHEMICAL PREPARATION AND PROPERTIES OF GALLIUM ARSENIDE OXIDE FILMS

Moscow ELEKTROKHIMIYA in Russian Vol 20, No 1, Jan 84
(manuscript received 9 Jul 82) pp 105-109

SOROKIN, I. N. and GAT'KO, L. Ye., Moscow Institute of Electron Technology

[Abstract] Details are presented on the preparation of gallium arsenide oxide films by low-temperature anodization of epitaxial layers of GaAs to form dielectric films. A key advantage of the electrochemical method is that the electrode process is self-limiting and ensures anodal oxidation of the semiconductor to a predetermined depth. Optimum characteristics of the anodal GaAs films are obtained when the thermal pretreatment is conducted at 620°K for 2 h which, although it reduces the breakdown voltage by 10-15%, markedly improves resistance to various solvents. The resultant value for the dielectric constant is 12.2 ± 0.3 with a film thickness of 90-120 nm, and refractive index of 1.82 ± 0.5 at a wavelength of 632.8 nm. At higher temperatures the dielectric constant and the breakdown voltage show a further decrease. Figures 5; references 14: 10 Russian, 4 Western.
[145-12172]

UDC 541.138.2:547

PHOTOELECTROSYNTHESIS OF ORGANIC COMPOUNDS ON TiO_2 ELECTRODE

Moscow ELEKTROKHIMIYA in Russian Vol 20, No 1, Jan 84
(manuscript received 10 Jan 83) pp 121-122

GRINBERG, V. A., DZHAVRISHVILI, T. V., VASIL'YEV, Yu. B., ROTENBERG, Z. A., KAZARINOV, V. Ye. and MAYOROVA, N. A., Institute of Electrochemistry, USSR Academy of Sciences, Moscow

[Abstract] Galvanostatic conditions were employed in evaluating the electro-photosynthetic potential of n- TiO_2 electrodes, using 12-15 mA current, 0.6 V, and mercury lamp illumination, at $24.0 \pm 3^\circ\text{C}$. In aqueous solutions of acetic, propionic and trifluoroacetic acids oxygen production ($2\text{OH}^- + 2\text{h}^+ \rightarrow 1/2(\text{O}_2) + \text{H}_2\text{O}$) was accompanied by a parallel process of carboxylate anion oxidation ($\text{RCOO}^- + \text{h}^+ \rightarrow \text{CO}_2 + \text{R}^\cdot$; $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{CF}_3$). In aqueous solutions acetic acid

yielded O_2 , C_2H_5 , CO_2 and CH_4 , while propionic acid yielded C_2H_4 , C_2H_6 , CO_2 and O_2 . In methanol propionic acid also yielded C_4H_{10} , in addition to the previously listed products. Photoelectrolysis of aqueous trifluoroacetic acid solutions resulted in the formation of CO_2 , CF_3H , C_2F_6 , CF_3COCF_3 and O_2 , while in 8:1 acetonitrile: water solutions CO_2 , C_2F_6 and CF_3H and O_2 were formed. In addition, the product yield of the Kolbe electrosynthetic reactions was markedly increased in methanol or water-acetonitrile solutions. The joint generation of $CH_3\cdot$ and $I\cdot$ radicals during photoelectrolysis of sodium acetate and sodium iodide (50:1) in aqueous solutions resulted in the formation of methyl iodide, among other products, indicating radical interactions. References 15: 6 Russian, 9 Western.
[145-12172]

FERTILIZERS

GRODNO ASSOCIATION EXCEEDS PLANNED FERTILIZER PRODUCTION

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 18 Dec 83 p 1

[Article by N. Kernoga, correspondent, Grodno]

[Text] Chemists of the Grodno Association "AZOT" imeni S. O. Pritytskiy are finishing outstandingly in the third year of the five-year plan. The three-year task of output of fertilizers they fulfilled as early as in November. The additional, above-plan, production was worth 26 million rubles. All of that additional output was accomplished by an increase in labor productivity. This indicator is considerably higher than in related enterprises. The "AZOT" also exceeds the control numbers of the five-year plan for manufacturing fertilizers (warranting the) Quality Label. Presently, 85 percent of the Association's output products bear the honorable Pentagon badge. This year the association is awarded a diploma of VTsSPS [All-Union Central Council of Trade Unions] and Gosstandart [State Standard] for this success.

12603

CSO: 1841/93

UDC 631.84.004.14(047)

EFFECTIVENESS OF USE OF NITROGENOUS FERTILIZERS, THEIR ROLE AND IMPORTANCE IN INTENSIFICATION OF AGRICULTURE

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 12, Dec 83 pp 724-727

KIL'MAN, Ya. I. and TOSHCHEV, A. F.

[Abstract] Use of fertilizer improves agricultural operations, since more than half of the harvest increase is due to fertilization. Developments in the Soviet Chemical Industry will continue expanding production of mineral fertilizers reaching for a goal of 150-155 million tons per year. Nitrogenous fertilizers are among the most important ones in agricultural application. During the past decade, Soviet production of nitrogenous fertilizers amounted to 20% of the world's output, a 100% increase from the preceding decade. As far as production per individual is concerned, USSR was already first in 1978. The principal users of N fertilizers are: Georgia, Uzbekistan, Tadzhikistan and Turkmenia. Their utilization is about as high as in foreign countries; however, in some areas deficiencies were noted. Therefore, new plants will be constructed to catch up. Economically speaking, each ruble of the fertilizer cost provides 2.5 rubles of the product. The liquid fertilizers appear to be most effective. The remainder of the paper was devoted to glorification of ammonium nitrate fertilizer. The USSR is a pioneer and leader in its industrial production. References 8 (Russian).
[120-7813]

UDC 661.53

GENERALIZATIONS OF EXPERIENCE GAINED DURING INVESTIGATION OF DEGREE ONE CONVERSION OF CARBON MONOXIDE IN AMMONIUM SYNTHESIS PLANTS WITH CAPACITY OF 1360 T/DAY

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 12, Dec 83 pp 733-735

FUREN, E. L., KOMOVA, Z. V., FINGEROVA, M. S., GORBACHEVA, N. B. and KOLESNIK, G. A.

[Abstract] One of the stages of ammonium production was analyzed: conversion of carbon monoxide of degree I; the authors compared imported plants with the equipment produced in the USSR. Technological aspects of both sources were comparable. After reciting comparative data, the conclusion reached was that

the Soviet-produced plant performed better than the imported plant. This was due to radial construction of domestic reactors providing a uniform gas flow in the catalyst layer and low resistance of the convertor. In domestic plants the catalyst lasted 6-8 years. In the imported convertors, the catalysts last about 4 years; their use is limited by increased resistance in the converter due to decomposition of the catalyst and inadequate gas flow distribution.

Figures 4; references 2 (Russian).

[120-7813]

QUALITY CONTROL IN NATURAL FOOD DYE PRODUCTION

Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 5, Sep-Oct 83 pp 37-40

RAKHIMKHANOV, Z. B., MUKHAMEDOVA, F. Kh., KARIMDZHANOV, A. K. and ISMAILOV, A.I.

[Abstract] A study was made of the effects of storage conditions on the stability of anthocyan dyes derived from plants and intended for use as food dye. The color of the dye solution in 0.1N HCl was compared with a standard ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) solution. Storage of the extracts of hollylock flowers at room temperature ($20-28^\circ\text{C}$) for 3 months showed a gradual disappearance of one of the anthocyan components and, beginning with the third month, the intensity of the color begins to decrease until 30% of the intensity is lost by the 9th month of storage. Storage under cellar conditions retards the onset of color loss by one month, reaching an 18.6% loss by the 12th month. Best results were obtained when the extracts were stored in the cold ($3-8^\circ\text{C}$); the qualitative and quantitative parameters of the extract did not change over a period of 12 months. Selection of the appropriate storage conditions appears to be an important factor in improving the productivity of natural dyes. References 7: 6 Russian, 1 Western.
[136-12172]

RED FOOD DYES FROM PLANTS

Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 5, Sep-Oct 83
(manuscript received 4 Jan 83) pp 46-49

RAKHIMKHANOV, Z. B., KARIMDZHANOV, A. K., ISMAILOV, A. I. and MUKHAMEDOVA, F. Kh.
Institute of Bioorganic Chemistry, Uzbek SSR Academy of Sciences

[Abstract] Several varieties of Central Asian plants were investigated as possible sources of anthocyanins to serve as natural red dyes for food. Analysis of hibisci (*Hibiscus* sp.), forest mallow (*Malva silvestris*), black and red hollylock (*Alcea niger* and *A. rosea*) and other plants showed that the anthocyan content ranged from 5.1-11.0%. The plants were extracted with 1.5% citric acid, the extract concentrated by evaporation and lyophilized. Removal

of pectins and other admixtures was achieved by treating the concentrate with 1.5 volumes of ethanol containing 0.5% citric acid. The inclusion of the acid also favors maximum color intensity since this parameter is pH dependent and is at a maximum at pH 2.0-3.0. References 10 (Russian).
[136-12172]

STRUCTURAL TRANSFORMATIONS IN THERMALLY-INDUCED INTRAMOLECULAR
CYCLODEHYDRATION OF POLYAMIDOHYDRAZIDES

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 1, Jan 84
(manuscript received 14 Apr 82) pp 32-35

BERESTNEVA, G. L., RUSANOV, A. L., BRONSHTeyN, L. M., MARIKHIN, V. A.,
MYASNIKOVA, L. P., ZHIZDYUK, B. I., CHEGOLYA, A. S. and KORSHAK, V. V.,
Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of
Sciences

[Abstract] Large angle, x-ray diffraction analysis was performed on the structures of polyamidohydrazides (PAH) and polyamido-1,3,4-oxadiazoles (PAOD), formed by thermally-induced intramolecular polycyclocondensation of PAH into PAOD. Studies on PAH ordered fibers and films demonstrated that greatest ordering is achieved with 1.5-fold stretching at 260°C, which represents the softening point of PAH. At that temperature PAOD formation is insignificant, while stretching of PAH at temperatures approaching the softening point of PAOD (ca. 320°C) is accompanied by PAOD formation. Formation of PAOD commences in the amorphous regions and does not involve the crystalline structure of PAH. Diffraction patterns of PAOD obtained by cyclization of PAH at 330°C followed by stretching at this temperature contain equatorial deflections present only in PAOD and indicate virtually 100% cyclization. The degree of orientation, however, was found to decrease as the temperature of the process increased. Superior structural parameters prevail when the temperatures of extrusion (320°C) and that of intramolecular polycyclocondensation (315°C) are quite close; the retention of considerable orientation is ascribed to diminished influence of relaxation processes. Figures 4; references 6:
4 Russian, 2 Western.
[141-12172]

UDC 539.194.536.27

SYNTHESIS OF O-ALKYL-N-(α -PIPERIDYL- β -PYRIDINE)METHYL PHOSPHONATES AND
O-ALKYL-N-(α -PIPERIDYL- β -PYRIDINE)METHYL THIOPHOSPHONATES

Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 5, Sep-Oct 83
(manuscript received 12 Nov 82) pp 40-43

ABDUBAKHABOV, A. A. and KASYMOV, Sh. K., Institute of Bioorganic Chemistry,
Uzbek SSR Academy of Sciences

[Abstract] Details are provided on the synthesis of two derivatives of the alkaloid nicotimine: O-alkyl-N-(α -piperidyl- β -piperidine)methyl phosphonates and O-alkyl-N-(α -piperidyl- β -pyridine)methyl thiophosphonates. The synthetic steps consisted of the reaction of dichloroanhydrides of methyl phosphonic and methyl thiophosphonic acids with primary alcohols to form the corresponding O-alkylmethylchlorophosphonates and O-alkylmethylchlorothiophosphonates, which were then reacted with nicotimine to give the two classes of target products. All of the reactions were conducted in the presence of triethylamine. The purity of the synthesized products was followed by TLC, and structural confirmation was obtained by IR and ESR spectroscopies. References 8: 6 Russian, 2 Western.
[136-12172]

UDC 548.737

STRUCTURE OF ORGANOPHOSPHORUS COMPOUNDS, PART 23: X-RAY ANALYSIS OF
MOLECULAR COMPLEXES INVOLVING TRIPHENYLPHOSPHINOXIDE AND TETRACHLORO-
PYROCATECHIN ($\text{Ph}_3\text{PO} \cdot \text{C}_6\text{Cl}_4(\text{OH})_2$) AND HYDRATED COMPLEX ($\text{Ph}_3\text{PO} \cdot \text{C}_6\text{Cl}_4(\text{OH})_2 \cdot \text{H}_2\text{O}$)

Novosibirsk ZHURNAL STRUKTURNOY KHIMII in Russian Vol 24, No 6, Nov-Dec 83
(manuscript received 3 Feb 82) pp 86-92

ANTIPIN, M. Yu., AKHMEDOV, A. I., STRUCHKOV, Yu. T., MATROSOV, Ye. I. and
KABACHNIK, M. I., Institute of Heteroorganic Chemistry imeni A. N. Nesmeyanov,
USSR Academy of Sciences

[Abstract] X-ray analysis was performed of 1:1 complexes formed between Ph_3PO and tetrachloropyrocatechin (TCPC), $\text{Ph}_3\text{PO} \cdot \text{C}_6\text{Cl}_4(\text{OH})_2$ (I), as well as the hydrated complex, $\text{Ph}_3\text{PO} \cdot \text{C}_6\text{Cl}_4(\text{OH})_2 \cdot \text{H}_2\text{O}$ (II). Both complexes were transparent triclinic crystals. Complex I consisted of two highly similar

crystallographic forms, in which each oxygen atom of the phosphoryl group formed two O ... H-O (2.611-2.689 Å)- type H bonds with the OH groups of one TCPC molecule, resulting in the formation of a nonplanar seven-membered 'chelate' ring. The presence of bonded water in II resulted in marked changes in the system of H bonds, with the formation of long chains of Ph_3PO , TCPC, and water molecules. All the active H atoms are involved in strong H bonds, the TCPC molecules form centrosymmetric dimers (O ... O, 2.795 Å) and their second H atoms form fairly strong H bonds with water molecules (O ... O, 2.597 Å). The water molecules serve as bridges between Ph_3PO pairs via hydrogen bond formation. Figures 2; references 13: 2 Russian, 11 Western. [138-12172]

UDC 542.91+541.69:547.1'118

ANTICHOLINESERASE PROPERTIES OF O-(ω -ALKOXYALKYL)-S-n-BUTYLMETHYLTHIO-
PHOSPHONATES, O-(ω -ALKOXYALKYL)-S-(BETA-ETHYLMERCAPTOETHYL)METHYLTHIOPHOS-
PHONATES AND THEIR METHYLSULFOMETHYLATES

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 11,
Nov 83 (manuscript received 28 Mar 83) pp 2473-2477

ABDUVAKHABOV, A. A., KHOLBEKOV, O. Kh., SADYKOV, A. A., GODOVIKOV, N. N. and
SADYKOV, A. S., Institute of Bioorganic Chemistry, UzSSR Academy of Sciences,
Tashkent; Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov,
USSR Academy of Sciences, Moscow

[Abstract] Study of the action on acetylcholinesterase and butyryl-
cholinesterase of O-(ω -alkoxyalkyls)-S-n- butylmethylthiophosphonates,
O-(ω -alkoxyalkyl)-S-(beta-ethylmercaptoethyl) methylthiophosphonates and their
methylsulfomethylates revealed that these compounds are potent irreversible
cholinesterase inhibitors. The presence of a hydrophilic O atom in the non-
splitting part of the inhibitor of the molecule promotes inhibition of
acetylcholinesterase but does not promote inhibition of butyrylcholinesterase.
Figures 3; references 6: 5 Russian, 1 Western.
[95-2791]

EQUILIBRIUM OF STEREOISOMERS OF 4,6-DISUBSTITUTED 2,5-DIPHENYL-2-BORA-1,3,5-DIOXAPHOSPHORINANES

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 11, Nov 83 (manuscript received 22 Mar 83) pp 2535-2541

ARBUZOV, B. A., YERASTOV, O. A., NIKONOV, G. N., ROMANOVA, I. P., ARSHINOVA, R. P. and OVODOVA, O. V., Institute of Organic and Physical Chemistry, Kazan Branch, USSR Academy of Sciences

[Abstract] Production of sulfides and selenides of 4,6-disubstituted 2,5-diphenyl-2-bora-1,3,5-dioxaphosphorinanes are described and discussed. The position of equilibrium and structure of their stereoisomers was determined. Figures 3; references 10: 9 Russian, 1 Western. [95-2791]

PRODUCTION AND SOME PROPERTIES OF DIPHENYLBORYLOXYMETHYL(METHYL)-PHENYLPHOSPHINE

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 11, Nov 83 (manuscript received 28 Mar 83) pp 2541-2545

ARBUZOV, B. A., YERASTOV, O. A. and NIKONOV, G. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, USSR Academy of Sciences, Kazan Branch

[Abstract] Methyl(phenyl)oxymethylphosphine was synthesized to produce an active P-C-O-B system and its reaction with isobutyl ether of diphenylboric acid was studied. Interaction of methyl(oxymethyl)phenylphosphine with isobutyl ether of diphenylboric acid forms 2,2,5-triphenyl-5-methyl-2-borane-5-phosphonine-1,3-dioxane which, upon distillation, splits off formaldehyde and gives diphenylboryloxymethyl(methyl)phenylphosphine which contains an active P-C-O-B system. Interaction of diethylaminomethyl(methyl)phenylphosphine with isobutyl ether of diphenylboric acid is achieved by intermediate hydride transport. References 9: 8 Russian, 1 Western. [95-2791]

SOME PROPERTIES OF PHOSPHORUS-CONTAINING ETHERS OF PHENYL- AND DIPHENYLBORIC ACIDS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 11, Nov 83 (manuscript received 28 Mar 83) pp 2545-2550

ARBUZOV, B. A., YERASTOV, O. A., NIKONOV, G. N. and ROMANOVA, I. P., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] Study of the complexing capacity of ethers of diphenylboric acid and cyclic ethers of phenylboric acid are described and discussed. Interaction of 1-diphenylboryl-3-oxopropane and diphenylboryloximethyl(oxymethyl)-phenylphosphinesulfide with amines produced stable crystalline complexes. Interaction of stereoisomers of 4,6-disubstituted 2,5-diphenyl-2-bora-1,3,5-dioxaphosphorinanes and their derivatives with pyridine depends upon coordination of the atom P but does not depend on the substituent on atom P (S, Se), its orientation or substituents on atoms C and conformation of the molecule. Interaction of 4,6-disubstituted 2,5-diphenyl-2-bora-1,3,5-dioxaphosphorinanes with selenium and methyl iodide depends upon the coordination of atom B. These results justify the practical conclusion that addition to the P-C-O-B system should readily occur in case of a simultaneous attack on atoms P and B.

References 8: 7 Russian, 1 Western.

[95-2791]

INTERACTION OF 2,4,6-TRIISOPROPYL-1,3,5-DIOXAPHOSPHORINANE WITH PHENYLAZIDE

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 11, Nov 83 (manuscript received 9 Mar 83) pp 2550-2554

ARBUZOV, B. A., YERASTOV, O. A., IGNAT'YEVA, S. N., ROMANOVA, I. P., OVODOVA, O. V. and ARSHINOVA, R. P., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences; Chemical Institute imeni A. M. Butlerov, Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] A study of the reaction of 2,4,6-triisopropyl-1,3,5-dioxaphosphorinane with phenylazide as a function of the ratio of reagents showed that 5-phenylamino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane and 5-phenylimino- and 5-phenylamino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane are formed. A stereoisomer with axial orientation of an amino group predominates in the equilibrium of 5-phenylamino-, 5-diethylamino-, 5-piperidino-, 5-morpholino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinanes and their sulfides. References 12: 10 Russian, 2 Western.

[95-2791]

o-CARBORANYL-CONTAINING ESTERS OF PENTAVALENT PHOSPHORUS ACIDS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 11, Nov 83 (manuscript received 12 Mar 83) pp 2640-2644

RYS, Ye. G., GODOVIKOV, N. N. and KABACHNIK, M. I., Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow

[Abstract] Newly developed methods of synthesizing carboranyl ethers of phosphinic acid, phosphonic acid and phosphoric acid from corresponding acetyl ethers, decarborane and dimethylaniline are described and discussed. References 6: 5 Russian, 1 Western. [95-2791]

CHLOROCYANIDES OF TRIVALENT PHOSPHORUS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 11, Nov 83 (manuscript received 24 Jun 83) p 2654

ROMANOV, G. V., NASMUTDINOVA, V. N. and PUDOVIK, A. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] It is reported that, during interaction of hydrogen chloride with cyanides of P(III), there occurs substitution of the cyanogroup by the chlorine atom and reaction with dicyanophosphines and dicyanophosphites yields compounds containing a chlorine atom and a cyanogroup simultaneously. The compounds obtained react with proton donor reagents and compounds containing multiple bonds. [95-2791]

PESTICIDES

UDC 615:547.552.43+564.307(088.8)

AMINE DERIVATIVES OF THIOUREA AND ISOTHIOCYANATES

Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 5, Sep-Oct 83
(manuscript received 14 Jan 83) pp 53-56

MIRAKHMEDOV, N. Sh., KIM, O. N., KASYMOV, Sh. K. and ABDUVAKHABOV, A. A.,
Institute of Bioorganic Chemistry, Uzbek SSR Academy of Sciences

[Abstract] Twelve new ethers of thiourea and isocyanate were synthesized to serve as pesticides and tested for effectiveness on the cotton-ball worm (*heliiothis armigera*), the orange whitefly, and the spider mite. The heterocyclic amine and alkaloid derivatives were found to be effective as acaracides to some extent. Particularly promising agents are phenylthiocarbamoyl-9-amino-acridine, benzoylthiocyanatephenyl-pyrazoline and diethyl aminoethylthiocyanate iodomethylate which, in a concentration of 0.1% were effective in killing 55-65% of the cotton-ball caterpillars. References 2: 1 Russian, 1 Western. [136-12172]

UDC 547.722.3'361.362.07:541.63:543.422.25

SYNTHESIS AND PROPERTIES OF TETRAHYDROFURYLACETYLENE ALCOHOLS

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian No 12, Dec 83
(manuscript received 27 Dec 82, after revision 11 May 83) pp 1602-1606

KARAKHANOV, R. A., VARTANYAN, M. M., SOLOV'YEVA, T. Yu. and LAPUKA, L. F.,
Institute of Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow

[Abstract] Details are provided on the synthesis of previously undescribed tetrahydrofurylacetylene alcohols (1-(tetrahydrofuryl-2)-propyn-2-ol-1, 1-(tetrahydrofuryl-2)butin-2-ol-1, 1-(tetrahydrofuryl-2)heptin-2-ol-1, 1-(tetrahydrofuryl-2)octin-2-ol-1, 1-(tetrahydrofuryl-2)-3-(phenyl-1)propyn-2-ol, 1-(tetrahydrofuryl-2)hepten-2-ol, 1-(tetrahydrofuryl-2)-3-(phenyl-1)-propen-2-ol-1) and certain of their acetates. Subsequent acetylation and hydrogenation of the alcohols to the tetrahydrofurylethylenes was accomplished with Lindlar catalysts. PMR spectroscopic data were tabulated and indicate that the alcohols exist as mixtures of diastereoisomers. References 9: 7 Russian, 2 Western. [123-12172]

SYNTHESIS OF THIIRANO-3,4-THIOLANE-1,1-DIOXIDE

Riga KHIMIYA GETEROTSIKlicheskih SOYEDINENIY in Russian No 12, Dec 83
(manuscript received 17 Feb 83) pp 1630-1632

BEZMENOVA, T. E., TUKHAR', A. A. BEZUGLYY, Yu. V., SLUTSKIY, V. I. and
NOSOVA, V. M., Institute of Physico-Organic Chemistry and Coal Chemistry,
Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Description is provided of the approach taken to the synthesis of
thiirano-3,4-thiolane-1,1-dioxide (I) by the reaction of triphenylphosphine
sulfide with oxirano-3,4-thiolane-1,1-dioxide in the presence of trifluoro-
acetic acid in benzene at 80°C for 60 h. The product, I, is a white
crystalline compound with a 157-159°C m.p., which is highly soluble in
ethanol, dioxane and acetone. IR and NMR spectroscopies were employed to
confirm the structure of I. References 8: 2 Russian, 6 Western.
[123-12172]

PETROLEUM PROCESSING TECHNOLOGY

CLEAN FUEL FOR KAMSK AUTOMOBILE PLANT

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 20 Jan 84 p 1

[Article by U. Bogdalov, Brezhnev, TASSR]

[Text] Yesterday, Urengoy gas reached the TETs [fuel power center] of the Kamsk Association for Production of Heavy Duty Automobiles and began to feed the power needs of the "Nizhnekamskneftekhim". Henceforth, mazut will not be burned in heating plant boilers. The air over the mountains of this powerful industrial region will become cleaner.

The 240 kilometers-long gas pipeline feeder has united the Kama area with the main line of Urengoy-Novopskov. A steel pipe, 1020 millimeters in diameter, intersected 14 water barricades and 120 underground communications, before it reached distributing stations in Brezhnev and Nizhnekamsk.

12473

CSO: 1841/137

RESEARCH ON MOTOR OIL FOR THE NORTH DISCUSSED

Moscow KHIMIYA I ZHIZN' in Russian No 1, Jan 84 p 38-41

[Article by Candidates of Chemical Sciences I. F. Radzevenchuk and S. Z. Kaplan (deceased): "Oil for the North"]

[Text] The high pace of the development of the energy and mineral resources of the northern and eastern regions of our country imposed special requirements upon machinery and vehicles. We need powerful cross-country vehicles, tractors, bulldozers, large-capacity dump trucks and other machines which would operate reliably in the most complicated conditions. It is necessary to maintain regular communication with remote construction sites, geological and drilling teams, cities and settlements. Such communication is unthinkable without reliable operation of aviation and automobile transportation facilities. And the reliability of the operation of any machine depends almost entirely on lubricating materials: motor and transmission oils and hydraulic fluids.

About two thirds of the territory of our country lies in cold latitudes. In the region of BAM [Baikal-Amur Railroad], in the Yakut ASSR, and in the northern area of Tyumen, the temperature drops to 40-50 degrees below zero, and sometimes even lower. But machines must be started easily and operate at any freezing temperatures. This depends primarily on lubrication.

The requirements imposed by modern machinery on motor oils and other lubricants are complex and sometimes contradictory. In order to start a cold motor without preheating, the lubricant must not be too thick and viscous at low temperatures. On the other hand, at high temperature which develops in modern powerful motors, it is necessary for the oil to remain sufficiently viscous, otherwise the lubricant does not lubricate properly. How can these two contradictory requirements be satisfied? But this is not all. We need oils which can be used in winter and in summer without changing, i.e., all-season oils. We need all-purpose oils which are suitable for various motors: for carburetor and diesel motors, as well as for transmissions. Finally, we need oils which retain their properties as long as possible in operation, i.e., oils for long-term operation.

On 18 June 1941, Professor P. P. Kobeko and his associate N. I. Shishkin sent to the "Journal of Technical Physics" their article which summarized their studies on the viscosity of liquids and colloidal solutions. The article "Principles of Obtaining Heavy Oils with a Low Temperature Dependence of Viscosity"

was published only in 1944 ("Journal of Technical Physics", Vol 14, No 1, 2, p 9) when the Red Army broke through the Leningrad blockade¹.

P. P. Kobeko and N. I. Shishkin sought the ways of creating lubricants with a high viscosity index (IV) an index which characterizes the behavior of the oil to a considerable degree, such as its starting and lubricating properties. This index is usually determined by comparing the oil being tested with two other standard oils. One of these standards has an ideally flat temperature curve (index 100), the other has a very bad one, the steepest curve (index 0). Thus, the goal of the researchers (just as that of their many predecessors) was to find a method of obtaining the so-called high-index lubricating materials (IV 90 and higher). The problem was complicated by the fact that it had to be solved from scratch: there were neither theoretical conceptions nor experimental data which could tell them which way to go.

Naturally, low-viscosity hydrocarbon liquids have a high viscosity index, as well as a low solidification point. However, they are not suitable as lubricants in their pure form: their viscosity is too low. More viscous oils have a steep temperature dependence. Nothing can be achieved by mixing such fluid and viscous oils: a solution of medium viscosity with a low IV is produced.

The following idea was proposed by P. P. Kobeko for obtaining high-index oils. If an insoluble powder is added to a low-viscosity liquid, then, due to a decrease in the free space in the volume of the liquid, the viscosity of the system increases substantially, but the temperature trend of viscosity remains the same. He was first to propose to dissolve in low-viscosity liquids polymers, the size of whose molecules (such as particles of a powder) is many times greater than that of the molecules of the solvent. At the very beginning of the 1950s, industrial production of such thickened oil was organized in our country: on the basis of petroleum distillates with addition of polyisobutylene as a thickener. Three years later, similar "wide-temperature" lubricants also appeared abroad.

At the present time, thickened oils occupy a leading place. For example, in the USSR they account for 75% of motor oils.

The idea of creating thickened oils looks extremely simple: a polymer thickener is added to a nonviscous base. However, in order to understand the behavior of such lubricants and their properties, one has to go deep into real physicochemical jungles.

The most important properties of thickened lubricants, i.e., their viscosity, its temperature dependence and stability, are connected primarily with the chemical structure and concentration of the added polymer (its usual concentration in oil is from 2 to 10%), its molecular mass, the composition of the oil base, interaction of the macromolecules with the solvent, and with the presence of other additives.

On solution, the macromolecules swell, their links (segments) are displaced in relation to the main chain, and the macromolecules changes its shape. Macromolecules can combine into associations, forming three-dimensional structural networks, and this unexpectedly and unpredictably increases the viscosity of the solution.

The polymer-solvent systems have a tendency toward stratification. This occurs both during cooling, and during heating. Each polymer solution has its own critical stratification temperatures (upper and lower). A homogeneous solution is possible only between these points. The width of the "safe" region between the critical temperatures depends on the chemical structure of the polymer and solvent, on the interaction between them, or on the value of the free energy of the thermodynamic system. But in practice, when it is necessary to develop a lubricating oil for a particular motor with particular properties, it is very important for the solution to be stable and not to separate at temperatures which develop on the piston rings of cylinders.

The temperature dependence of the viscosity of a polymer solution is the main characteristic for oils used in cold regions and is determined by the energy which has to be spent on the movement of the segments of the molecules. Polymers with nonrigid, flexible molecular chains make it possible to create thickened oils with flat temperature characteristics and high viscosity indexes.

Finally, the viscosity of a thickened oil does not only depend on its own properties, but also on the speed of the moving surfaces being lubricated, or on the so-called sliding velocity. When it increases, the associations of the polymer macromolecules and their spatial structures are destroyed, and the molecular chains become oriented in the direction of the acting force. It is clear that this decreases the viscosity of the solution. When the speed decreases, the polymer structure, as well as the viscosity, are restored.

This phenomenon of temporary decrease of viscosity, or viscosity anomaly, occurs particularly at low temperatures. It goes without saying that it helps us in solving our problem of developing effective lubricants for the North. Oils in which the viscosity anomaly occurs (for example, oils thickened with polymethacrylate) make it possible to start motors easily at very low freezing temperatures, are pumped well in lubrication systems, lower friction in friction assemblies and, therefore, yield a considerable saving in fuel. When driving with frequent stops in the city or in the area of an enterprise, the saving in fuel can reach 10%.

Modern thickened oils are made on the basis of petroleum distillates from which light head fractions and tail fractions are removed; the former can evaporate during the operation of the motor, and the latter leave carbon deposits. Aromatic and naphthenic hydrocarbons, whose molecules consist of cycles with long hydrocarbon chains, as well as isoparaffins make oil bases sufficiently viscous. However, petroleum does not contain sufficient quantities of these natural components and, therefore, the initial petroleum products are subjected to additional thermocatalytic treatment in the presence of hydrogen.

Synthetic oils, for example esters of dibasic acids (adipic, sebacic) with monatomic higher alcohols or esters of polyols with fatty acids can serve as a basis for thickening. Such substances are stable to oxidation in motors and, which is particularly important for arctic lubricants, solidify at a very low temperature. However, they are still quite expensive and our petrochemical industry is only starting their industrial production.

The most popular additives used for increasing viscosity are hydrocarbon polymers (polyisobutylene, ethylene-propylene and styrene-isobutylene copolymers, etc) and oxygen containing polymers (polymethacrylates, polyacrylates, polyvinylbutyl esters). Their molecular mass usually lies within the limits from 10,000 to one million, although oligomers with a molecular mass from 500 to 6000, which are more stable against mechanical destruction, started being used in recent years as viscosity additives.

The complex set of additives to which the creators of thickened oils resort more and more frequently, makes it possible not only to increase the viscosity index, but also to manipulate other important properties of lubricants. For example, some additives serve as depressing agents, lowering the solidification temperature of the oil; others give it detergent properties and the ability of not only lubricating friction surfaces, but also to remove carbon deposits from them.

Finally, it is also necessary to have such additives which would protect oils in operation under particularly difficult conditions such as in highly accelerated engines and stressed transmissions, against decomposition and oxidation, mechanical and thermal-oxidative destruction of polymers. A new method has been proposed very recently for the protection of lubricating materials: to thicken oils with such viscosity additives which form antioxidants themselves. For example, copolymers of butylene with styrene derivatives have such properties: during oxidation, they form phenols which inhibit subsequent oxidation reaction. Such additives, so to speak, stabilize themselves.

Professional and amateur drivers, evidently, quite often used in their engines oils with names consisting of numbers and letters which included a small letter "z". This is a notation for thickened oils² which are used more and more every year instead of the common lubricants. They are replacing them due to their truly unique properties. Here is just one example.

Motor pools serving enterprises and construction sites of the northern areas started receiving a new transmission oil, TSz-9gip, developed by a team of researchers headed by N. V. Shchegolev. The mixture of a low-viscosity (MS-8) and viscous (MC-20) oils was thickened with a polymer with a molecular mass of 4000. It contains antiwear and antiscaff additives, a depressing agent, and corrosion inhibitors. This lubricant makes it possible to start a vehicle without any preheating and drive it at minus 55 degrees C. One who happened to drive a vehicle in cold weather, not even a truck but a passenger car and not even in the Extreme North but in relatively moderate conditions of the Moscow or Leningrad winter, knows what this means. Due to the new arctic lubricant, hydraulic losses in the transmission decrease and the transmission efficiency of the automobile "Ural-375" increases by 8-9% in comparison with its operation on the best unthickened oils.

The high viscosity index and the high mechanical and thermal-oxidative stability of thickened oils make it possible to drive in winter and summer without changing the lubricant: they are all-purpose and all-season oils. It goes without saying that this property of such oil greatly facilitates the servicing of vehicles, particularly in the difficult conditions of northern regions. Thickened oils, in many respects, bring us closer to the engineering ideal: machines which

do not require any servicing. The fact is that even today it is possible to develop lubricants with additives which lose their effectiveness extremely slowly during the operation of a machine. Recently, road tests were conducted for a synthetic oil thickened with polymethacrylate. After a 40,000 km run, the viscosity of the lubricant increased only by 25%, i.e., essentially, remained within the operational limits. In the meantime, such a drive doubles the viscosity of a common oil, i.e., makes it totally unfit for further use.

Studies on the kinetics and rheology of polymer solutions and on the processes of thermal, oxidative and mechanochemical destruction of molecules are continuing. It can be stated confidently that the time is not far distant when vehicles will run 125,000, 130,000 kilometers without any oil change.

Footnotes

1. KHIIMIYA I ZHIZN' had a detailed report on Pavel Pavlovich Kobeko's (1897-1954) work at the Leningrad Physicotechnical Institute during the years of the Second World War (1974, No 8-10) -- Editor.

2. The brand names of modern oils contain other important information. For example, M-62/10V oil used in diesel and carburetor engines is well known at motor pools. Its brand name means: M -- motor; 6 -- viscosity at -18°C (in reference units); 10 -- kinematic viscosity at 100°C (mm²/s); V -- universal for medium-accelerated engines.

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10,233

CSO: 1841/121

ORENBURG HELIUM-PRODUCING PLANT QUALITY TESTED

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 16 Dec 83 p 1

[Article by G. Zazvonov, Orenburg]

[Text] Testing of new capacities at the helium plant in Orenburg is nearing completion. When implemented, the production of helium concentrate will triple.

A steel cigar 10 meters in diameter has risen to a height of an 18-story building. It is surrounded with a metallic bookcase-like skeleton. This is the new unit. It has been built by organizations of the Minerrestroy and Minmontazhspetsstroy unions. All of the basic construction and assembly jobs were carried out by the contract-brigade method.

Very great is the responsibility of the creators of the complex technological assembly. Pressure inside the system rises to almost 100 atmospheres and temperature drops to minus 186° (Celsius). Therefore, requirements regarding the quality of pipeline joints are unusually severe. Inspection with X-rays has shown that brigades of I. Putintsev, A. Gorbunov and others did their job perfectly. Experts from trusts "Uralmontazhavtomatika", "Orenburg-neftekhimmontazh" and "Uralelektromontazh" are also confirming their high expertise. They take part in the start-up and adjustment tasks as well.

At the end of the present year the powerful unit will be brought into operation. It will process several million cubic meters of natural gas a year. Helium concentrate will go from here to scientific laboratories, electrical engineering enterprises and machine-building plants for testing newly created materials and devices.

12603

CSO: 1841/93

UDC 629.7.036:62.192

ASSURANCE OF CHEMOMOTOLOGIC RELIABILITY IN AVIATION TECHNOLOGY

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 12, Dec 83 pp 6-8

PISKUNOV, V. A., ZRELOV, V. N. and MIKHEICHEV, P. A.

[Abstract] Economy of fuel and energy resources represent one of the major government concerns. An important role in solving the problems is played by chemomotologic reliability of aviation technology (AT) leading to rational utilization of fuel. On the basis of past experience and special studies, a system was developed for predicting chemomotologic reliability of AT based on three tasks: 1) optimization of construction: use of wear and corrosion resistant materials, more effective combustion; 2) optimization of the quality of fuels and oils: technical-economical rationalization of the quality of fuels and oils, improved technological processes and quality control, and 3) optimization of the use of airplane engines. Effective use of petroleum crude should take into consideration some techniques applied abroad to utilization of the fuel with a wide range of composition, which is not utilized within the USSR. Chemomotologic reliability of AT should be considered at the earliest possible time; at the design stages of AT. References 3 (Russian).
[107-7813]

UDC 621.892.339.443

RATIONAL UTILIZATION OF PETROLEUM PRODUCTS IN AVIATION TECHNOLOGY

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 12, Dec 83 pp 8-9

BEDRIK, B. G., NOVOSARTOV, G. T., UGRYUMOV, V. S., AGAPOV, P. N.,
KRICHINSKIY, I. S. and TARAKANOVA, T. D.

[Abstract] The problems of national utilization and economy of petroleum products must be solved at all stages: in production, in transportation, storage and in utilization. The present paper reports generalizations projected on the basis of a series of studies aimed at rational use and economy of petroleum products in use and service of aviation technology (AT). To assure reliable operation of motors, the oil change periodicity must be considered; this aspect has great economic impact. Normal patterns based on traditional concepts or on calendar convenience should be replaced by evaluations of qualitative composition of "special" oil. The cited studies should be continued and expanded to provide additional data on optimization of operational characteristics of both the equipment and lubricants. References 5 (Russian).
[107-7813]

CHARACTERISTICS OF DIESEL PERFORMANCE ON AQUEOUS-FUEL EMULSIONS

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 12, Dec 83 pp 12-14

TSENEV, V. A., VZPI [possibly All-Union Correspondence Polytechnic Institute]

[Abstract] The principal goal of this study was to achieve decreased heat strain of diesel engines resulting from addition of water to the fuel and to increase their economic utilization by improving the mixing process and combustion. In addition, the use of heavy fuels and fuels mixed with various additives was studied. To produce stable finely-dispersed aqueous-fuel emulsions, ultrasound technique was applied. Even this did not provide for stability of the emulsified state; therefore, surfactants had to be added to the system. Extensive experimental data are reported on the evaluation of diesel fuels mixed with water. In order to prevent corrosive processes from occurring in the engine, it is recommended to convert to pure diesel fuel during the last few minutes of the operation of a diesel engine. Figures 4; references 3 (Russian).

[107-7813]

EXTENSION OF DIESEL FUEL RESOURCES BY OPTIMIZATION OF MAZUT F-5 COMPOSITION

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 12, Dec 83 pp 14-15

SEREGIN, Ye. P., GORENKOV, A. F. and BUGAY, V. T.

[Abstract] Mazut F-5 is an all season fuel for boiler plants and for medium and slow revolving diesel engines used in sea and river navigation. The use of Mazut is restricted by its low temperature properties. To enlarge its utilization, diesel fuel was added in various proportions. To decrease the use of diesel fuel, Mazut components were studied in respect to their performance under conditions of low temperature. It was established that the quantity of diesel fuel in Mazut F-5 depends on the content of residual material above 500°C. Increasing the content of this residue by the use of vacuum distillation of Mazut will lead to a 25% reduction of diesel fuel consumption in Mazut F-5. Figures 3; references 5 (Russian).

[107-7813]

DETERMINATION OF ILLUMINATION INTENSITY OF REACTIVE FUEL FLAMES

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 12, Dec 83 pp 19-20

GORODETSKIY, V. G., GUTENEV, B. S. and ZLYDAREV, S. S.

[Abstract] A new method was developed for determination of fuel combustion in reactive engines. The method was based on determination of the intensity of light emission (ILE) of a reactive fuel flame jet in a miniature gas turbine engine. Based on this engine, an apparatus was developed for determination of the carbon-deposit-forming properties of various fuels. A photoelectronradiometer was used to register ILE, whose sensitivity was higher than that of the thermoelectric radiometer by an order of magnitude. The fuels studied could be arranged in the following order of increasing ILE: RT, TS-1, T-6, T-1.

Figures 2; references 6 (Russian).

[107-7813]

CHARACTERISTICS OF DETERMINATION OF OCTANE NUMBERS IN AQUEOUS FUEL EMULSIONS

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 12, Dec 83 pp 22-23

BORISOV, Yu. A., NIKITIN, I. M. and PROSTOV, V. N., Moscow Physical-Technological Institute

[Abstract] Results were reported of the determination of active number of standard fuels emulsified with water (mixtures of isooctane and n-heptane) and stabilized with various surfactants. As a result, new fuels were obtained, even though at present it is very difficult to obtain a stable water-gasoline emulsion. In this study, pentol, OP-4 and Tween -80 stabilizers were used to lower the water-hydrocarbon interphase tension. It was shown that addition of surfactants had little effect on combustion processes. With increased water content in the emulsion, the octane number increased. It was concluded that the antidetonation effect of water did not depend on the method of fuel supply to the engine, when it was completely evaporated prior to firing the mixture. To make practical recommendations, more studies on specially developed equipment are necessary. Figures 2; references 10: 8 Russian, 2 Western.

[107-7813]

PROGNOSTICATION OF PERFORMANCE LIFE OF AVIATION OILS BASED ON RESULTS OF LABORATORY EXPERIMENTS

Moscow KHEMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 12, Dec 83 pp 23-25

FEDOROV, Ye. P., GORYACHEV, V. V. and ZAPOROZHSKAYA, O. A.

[Abstract] Reliable performance of aviation engines depends to a large extent on proper selection of oils and scientifically-determined schedules of oil changes. Proper engine lubrication will be assured if during the entire service none of the indices of efficiency exceed the maximum permissible levels. Selection of such indices and determination of maximum tolerance is a complex scientific-technical problem which must be solved by a combination of laboratory and field studies. The principal oil properties affecting the performance of engines are: thermooxidative stability, lubricating ability, corrosive aggressiveness and low temperature properties. Laboratory tests showed that inhibitors can not always determine the reliability of oils. On the basis of laboratory results of ten lubricants, methods were developed for determination of maximum indices of physical-chemical and performance properties, as well as the duration of reliable performance. The different variations consisted of analysis of the starting oil, oxidation on the SH-3 apparatus and determination of the performance life. References 2 (Russian).
[107-7813]

RHEOLOGICAL PROPERTIES OF REACTIVE FUELS

Moscow KHEMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 12, Dec 83 pp 25-27

LIKHTEROVA, N. M., GORENKOV, A. F. and PEREPELKINA, O. A.

[Abstract] Low temperature fluidity of reactive fuel is evaluated by two indices: initial crystallization temperature and kinematic viscosity at -40°C . Rheological properties of various fuels were determined on a rotational viscosimeter Reostat-2 in the temperature range from -30°C to -65°C . Cooling the fuel down to the temperature of initial crystallization follows a smooth sloping curve. The steepest curves represented mixtures of cyclanes with alkanes, the flattest--corresponded to cyclanes. Alkanes appeared to have the strongest effect on the increase of viscosity of these fuels during the cooling process. It was concluded that at low temperature the fluidity of reactive fuels with initial crystallization temperature of -50°C should be determined by standard indices as well as by dynamic viscosity and by the presence of the maximum shearing stress. Figures 3; references 6: 5 Russian, 1 Western.
[107-7813]

OXIDIZABILITY OF REACTIVE FUELS T-6 AND RT DURING PROLONGED STORAGE

Moscow KHIMIYA I TEKHNOLOGIYA TOPLIV I MASEL in Russian No 12, Dec 83 pp 27-28

VESELYANSKAYA, V. M., RADCHENKO, Ye. D. and ENGLIN, B. A., All-Union Scientific Research Institute of Petroleum Processing

[Abstract] The difference in the oxidation rates of various fuels is probably due to different contents of antioxidants. To verify this assumption, adsorption resins were removed from the fuels RT and T-6 by passing them through activated aluminum oxide. The data obtained showed that T-6 fuel has lower tendency to oxidize than RT. This difference is due to different content of antioxidative additives. Therefore, it was concluded that, in order to assure prolonged storage of fuels, they should be stabilized with effective antioxidants. References 5 (Russian).

[107-7813]

PREPARATION CHARACTERISTICS OF AQUEOUS-FUEL EMULSIONS FOR DIESEL ENGINES

Moscow KHIMIYA I TEKHNOLOGIYA TOPLIV I MASEL in Russian No 12, Dec 83 pp 30-31

ANTONOV, V. N., Omsk Agricultural Institute imeni S. M. Kirov

[Abstract] During the emulsification process two distinct phases predominate: fractionation of the dispersing phase into small droplets and stabilization of these droplets in the dispersing medium. Emulsion designed for diesel engines should be of the "reverse" type, meaning "water in oil". This assures adequate ignition and combustion. The use of direct emulsion, i.e., "oil in water" may lead to many complications in the equipment or in the combustion process itself. Several surfactants were used in studying aqueous-fuel emulsions without satisfactory results; none of them led to formation of stable emulsions. The authors reported data on 10 preparations used in studies designed to develop adequate emulsions, without mentioning the reagents; a claim was made of obtaining aqueous-fuel emulsions with required stability. In such emulsions the hydrophylic part of the emulsifier dissolved in water and the hydrophobic--in the fuel. Figures 5; references 7 (Russian).

[107-7813]

DECREASE IN FUEL CONSUMPTION USING SPECIAL ADDITIVES TO MOTOR OILS

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 12, Dec 83 pp 33-35

LASHKHI, V. L., CHECHETKIN, V. V. and KULAGIN, V. V.

[Abstract] To increase rational use of petroleum products, a search was made for new methods of lowering the consumption of fuel for internal combustion engines. One of the approaches concentrated on lowering the friction between various engine parts. This could be achieved by using special lubricants or lubricants with added modifiers. One of the most promising additives is an oil-soluble molybdenum additive. The remainder of this paper was devoted to review of accumulated literature data on this additive. In concluding statement an appeal was made for extensive studies in this field of practical investigations. References 44: 28 Russian (18 by Western authors), 16 Western. [107-7813]

GROWING DEMAND FOR DIESEL FUEL

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 1, Jan 84 pp 6-8

ENGLIN, B. A., MITUSOVA, T. N., PEREZHIGINA, I. Ya. and AFANAS'YEVA, Ye. A.,
All-Union Scientific Research Institute of Petroleum Production

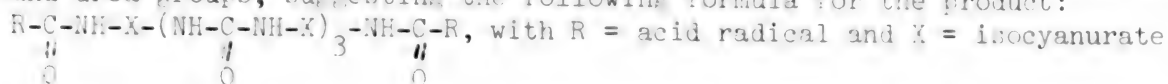
[Abstract] An analysis of the increasing need for diesel fuels has led to the conclusion that further demands must be met by expanding the distillation of the kerosene-gasoline fraction of residual fuels. Concomitantly with the increased output of diesel fuels the Soviet capacity for producing pour-point depressants will have to be enlarged to approach the level at which they are produced abroad. At the present time, Soviet capacity for pour-point depressants remains inadequate and the available capacity for producing diesel fuel cannot be fully exploited. Any serious expansion of diesel fuel supply in the USSR will depend on increasing the output of pour-point depressants. [133-12172]

LUBRICATING GREASE WITH AMIDOISOCYANURATE THICKENER

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 1, Jan 84 pp 24-25

DANILOV, A. M., SERGEYEVA, A. V. and SINITSYN, V. V., EF [expansion unknown, possibly branch of main institute] All-Union Scientific Research Institute of Petroleum Production

[Abstract] Description is provided of the properties of a lubricant grease prepared by the reaction of 2,4-toluylenediisocyanate and higher fatty acids in the presence of alkali metal acetate catalysts at 140-170°C. IR spectra indicated isocyanate trimerization and concomitant formation of amide bonds and urea groups, suggesting the following formula for the product:



fragment. Following thickening with amidoisocyanurate and oil I-20A a yellowish or light-brown lubricant was obtained, which offered high colloidal stability, considerable freezing resistance, and good wear protection. However, further improvements will have to be made in the formulation for this lubricant to offer satisfactory corrosion protection for ferrous and nonferrous metals. Figures 2; references 6: 5 Russian, 1 Western.

[133-12172]

EVALUATION OF THERMOOXIDATIVE STABILITY OF AVIATION ENGINE OILS ON APPARATUS OP-100

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 1, Jan 84 pp 29-30

CHVYKOVA, Ye. N., ZAPOROZHSKAYA, M. A., MORYACHEV, V. V. and FEDOROV, Ye. I.

[Abstract] Cursory description is provided of an apparatus, OP-100, [USSR Author's Certificate No 744325] designed for testing the susceptibility of natural and synthetic oils used in aviation gas turbines to thermal oxidation. OP-100 is designed to heat the oil sample either in bulk volume by percolation of air through a layer of the oil, or as a thin film exposed to contact with a heated metal surface. Testing of several oil samples at temperatures ranging from 150 to 320°C for 3 to 50h with subsequent standard physicochemical analyses resulted in the following ranking: MK-3<MK-8p<MS-8p and 36/LKu-A<E-3V<LZ-240. The results were in agreement with standard techniques used in inducing thermal oxidation of aviation motor oils. Figures 1.

[133-12172]

EFFECTS OF POLYMERIC ADDITIVES ON THICKENED OILS

Moscow KHEMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 1, Jan 84 p 34

KULIYEV, A. B., KULIYEV, F. A. and IMANOVA, G. I., Institute of Chemical Industry, Azerbaijan SSR Academy of Sciences

[Abstract] Certain of the advantages of the multifunctional oil additive IKhP-234 developed at the Institute of Chemical Industry (IKhP), Azerbaijan SSR, are delineated. Testing with various other detergent and dispersing additives demonstrated that IKhP-234 markedly improved thermal tolerance, wear protection, viscosity, and anticorrosive characteristics of the oil samples. IKhP-234 has been approved for addition to the All-Union motor oils in groups M-4z/8V₁ and M-4z/V₂, and to the all-season hydraulic fluids M-21KhP and M-31KhP intended for industrial tractors.

[133-12172]

UDC 615.282:547.241].012.1

SYNTHESIS OF POTENTIAL DRUGS BASED ON HYDROPHOSPHORYLIC COMPOUNDS, PART 4:
SYNTHESIS AND ANTIMYCOTIC ACTIVITY OF UNSATURATED ORGANOPHOSPHORUS COMPOUNDS

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian No 12, Dec 83
(manuscript received 29 Mar 83) pp 1448-1453

YUDELEVICH, V. I., BELAKHOV, V. V., BELYAYEVA, T. N., SERGIYENKO, L. V.,
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[Abstract] Some unsaturated phosphonates, polymer compounds based on some of them, phosphinates and phospholenes were synthesized and studied to determine their potential for use as antimycotic drugs. Most of the compounds were found to be only slightly active, especially in regard to the most common fungus diseases caused by *C. albicans*, *C. tropicalis* and *Cr. neoformans*. Ammonium salts of several phosphonous acids, containing a phosphorus-hydrogen bond were somewhat more active than cited phosphinic acids and their salts. Isobutyl and isoamyl ethers of two prepared propenephosphinic acid possessed antimycotic activity both in respect to yeast-like fungi and also, in respect to pathogenic organisms such as *Hor. pedrosoi*, *Emm. crescens* and *Pen. granulatam*. The study showed the promise of the compounds studied as antimycotic drugs. References 11: 10 Russian, 1 Western.
[110-2791]

UDC 615.104.41.017:615.28

COMPARISON OF ANTIMICROBIAL ACTIVITY OF SOVIET-PRODUCED PRESERVATIVES

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian No 12, Dec 83
(manuscript received 21 Sep 83) pp 1498-1501

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[Abstract] Study of antimicrobial properties of some Soviet drug preservatives in relation to *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis*, *Candida albicans* and *Aspergillus niger* B.

examined the preservatives in the following concentrations: nipagin-nipazol (4:1), 0.2 percent; sorbic acid, 0.2 percent; benzalkonium chloride, 0.1 percent, and ethonium, 0.02 percent and 0.2 percent. The following classification of the preservatives was made: nipagin-nipazol is slow acting (24 hours and more with respect to *Bac. subtilis*; sorbic acid is quick acting (from 10 to 60 minutes) against *Ps. aeruginosa*, *E. coli* and *Bac. subtilis* and slow acting (24 to 48 hours) against *C. albicans*, *Asp. niger*, *Staph. aureus* and *Bac. subtilis*; benzalkonium chloride is quick acting (10 to 60 minutes) against *Staph. aureus* and *Bac. subtilis* and slow acting (24 to 48 hours) against *C. albicans*, *Asp. niger* and *Bac. subtilis* and very slow acting (72 to 120 hours) against *E. coli* and *Ps. aeruginosa*; ethonium is quick acting (10 to 60 minutes) against *Staph. aureus*, *Ps. aeruginosa*, *E. coli*, *C. albicans* and *Bac. subtilis* cells, slow acting (48 hours) against *Bac. subtilis* spores and inactive (more than 168 hours) against *Asp. niger* even at very high concentrations. Ethonium can be used as a preservative to protect mild drugs from microbial contamination during storage. References 16: 7 Russian, 9 Western.
[110-2791]

UDC 615.33.012.6

AUTOMATIC BATCHER OF NUTRIENT MEDIUM COMPONENTS IN PROCESSES FOR REGULATING ANTIBIOTICS BIOSYNTHESIS

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian No 12, Dec 83
(manuscript received Oct 82) pp 1507-1510

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[Abstract] A device which implements fixed functions and the algorithm of control of an automatic batching process and possible applications of it are described and discussed. The technological diagram of the batching process is presented and the structural diagram of the control device is described. The device ensures reception from a computer or an operator of a command for input of additive to a specific fermenter and implementation of the command in real time according to the fixed algorithm of control. It can service up to 20 fermenters. Figures 2.

[110-2791]

NEW APPROACH TO SYNTHESIS OF 2-AMINOMETHYL-3-PHENYL-5-NITROINDOLE DERIVATIVES

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian No 12, Dec 83
(manuscript received 9 Feb 83, after revision 22 Jul 83) pp 1648-1651

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[Abstract] Previously-undescribed derivatives of 2-aminomethyl-3-phenyl-5-nitroindole were synthesized by the bromination of 2-methyl-3-phenyl-5-nitroindole derivatives to give 2-bromomethyl-3-phenyl-5-nitroindoles, which were converted to the 2-aminomethyl- derivatives via the Delépine reaction. Hydrolysis of 1-methyl-2-bromomethyl-3-phenyl-5-nitroindole gave 1-methyl-2-hydroxymethyl-3-phenyl-5-nitroindole, and the latter was oxidized by chromic anhydride to the 2-formyl derivative of indole. The latter was aminated via the Leuckart-Wallach reaction to 1-methyl-2-aminomethyl-3-phenyl-5-nitroindole. The structures of the various compounds were confirmed by IR, ESR and mass-spectroscopic data. References 13: 4 Russian, 9 Western.
[123-12172]

Moscow KHIMIYA I ZHIZN' in Russian No 1, Jan 84 pp 25-29

[Article by Doctor of Chemical Sciences M. L. Khidekel' and L. M. Gol'denberg]

[Text] Metals possess many remarkable properties: malleability and plasticity, hardness and heat and corrosion resistance; they are characterized by high heat and electric conductivity; many metals and their alloys become superconductors at a very low temperature, i.e., cease to conduct electric current.

Since ancient times people have been perfecting the methods of the extraction and processing of metals and their alloys trying to obtain materials with new and more advanced properties which would satisfy practical needs. Polymers have somewhat shaken the belief that metals are irreplaceable: modern synthetic materials not only compete successfully with metals, but sometimes even they themselves are irreplaceable.

Until recently it seemed unlikely that it would be possible to synthesize a material possessing one of the main properties of any true metal: high electric conductivity which increases with a drop in temperature. It was even more difficult to imagine that some day it would be possible to create a nonmetallic superconductor.

Nevertheless, the problem was solved in the last ten years: synthetic metals have been obtained (including those possessing the properties of superconductors). These are primarily the so-called charge-transfer complexes and ion-radical salts formed by organic, coordination and polymer compounds.

Secrets of Forgotten Substances

Alchemists synthesized many substances in their attempt to make gold. Some of them became common reagents in modern chemistry. However, evidently, most of the products of the experimental efforts of alchemists was undeservedly forgotten. At the same time, it is not excluded that many substances produced by alchemists could be of interest for science in our times.

In 1974, a group of Canadian chemists started studying the so-called "alchemists' gold", a product that had the same color as gold, but, of course, had nothing

in common with it. It was established that one of the compounds contained in this product had the composition $\text{Hg}_{2.86}\text{AsF}_6$. The result of the study of this compound was sensational: a compound known for at least three centuries turned out to be... a synthetic metal with a conductivity of $8000\text{ Ohm}^{-1}\text{ cm}^{-1}$! Mercury forms in it polymer chains with metal-metal bonds, and the distance between the Hg atoms is equal to 2.64 \AA , which is substantially less than in the metallic mercury (3.005 \AA).

As early as 1810, tetracyanoplatinate salts $\text{K}_2\text{Pt}(\text{CN})_4\text{Cl}_{0.3}\cdot 3\text{ H}_2\text{O}$ and $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}\cdot 3\text{ H}_2\text{O}$ were synthesized. It was only in recent studies conducted by the Institute of Chemical Physics of the USSR Academy of Sciences that it was established for the first time that these complexes are conductors which transform to superdielectrics, substances with an unusually great dielectric constant when the temperature drops. Together with the recently obtained analogous compounds possessing the electrophysical characteristics of metals, they became an object of numerous studies by scientists of various countries.

In 1910, an inorganic polymer, polythiazyl $(\text{SN})_x$ was synthesized; only many years later it was revealed that this polymer has semiconductor properties. In 1972, while analyzing the prospects of obtaining superconductors on the basis of polymeric compounds the members of the Institute of Chemical Physics pointed out the necessity of studying crystalline polythiazyl as a possible synthetic metal; in fact, in 1973, a group of American physicists showed that crystals of this strongly anisotropic polymer exhibit a metal-type conductivity, and in 1975, it was found that $(\text{SN})_x$ changes to a superconductor state at 0.26 K .

As we can see, there was not a single organic compound among these first representatives of synthetic, or molecular, metals. There arises a question: was this accidental?

In the inorganic world, the metallic state is a common phenomenon: it is characteristic of three quarters of all simple substances formed by the elements of the periodic system, some of their derivatives and many alloys. This is explained by the fact that electrons in such compounds are capable to freely moving over the crystal lattice, forming the so-called "electron gas", which creates the metal-type of conductivity.

On the contrary, the metallic state was not observed in the world of organic compounds prior to recent investigations in spite of numerous attempts. A high metal-type conductivity which was ensured by a developed system of conjugate pi-electrons was discovered relatively long ago with respect to the aromatic rings of graphite; nevertheless, organic (including coordination and polymer) substances are dielectrics or, at best, semiconductors; electric conductivity of organic substances most frequently does not exceed $10^{-17}\text{ Ohm}^{-1}\text{ cm}^{-1}$. The valence electrons of organic molecules are not too inclined to leave their long-occupied places...

The attempts of obtaining synthetic metals through the displacement of organic radicals by metals, for example, from aliphatic halides, are an interesting part in the history of organic chemistry. From the viewpoint of the modern concepts, these studies were based on the hope that unpaired electrons of free organic radicals will be sufficiently mobile in the solid phase.

However, the first attempts of this kind led to a different result -- to the discovery of new organic reactions: free radicals doubled uncontrollably, and their unpaired electrons were again involved in stable covalent bonds. Subsequent syntheses of stable free radicals did not yield anything new in this sense: as a rule, these substances turned out to be paramagnetic dielectrics and not organic metals, although some of them had the characteristic metallic luster (for example, α , α -diphenyl- β -picryl-hydrazyl). There was nothing to be done: the unpaired electrons stubbornly localized on individual molecules, and refused to move in the solid phase.

It seemed that a solid basis was created for pessimism...

Problems and Solutions

The approach to the solution of the problem of synthesis of organic metals was complex and long. Success was not achieved immediately; it was preceded by the development of theoretical and experimental principles of obtaining organic semiconductors carried out jointly by scientists of many countries of the world (USSR, U.S.A., Japan). These studies led to the synthesis of a number of practically important semiconducting materials of organic nature; the chemistry and physics of organic semiconductors also opened the way to a new understanding of certain biological phenomena.

At the same time, the synthesis of organic semiconductors had also a stimulating effect on the search for organic metals and superconductors. For example, in the beginning of the 1960s, investigations by U. Little became particularly popular among chemists. He suggested that in some organic macromolecules (specifically, in long polymer chains having a developed system of conjugated bonds and carrying fragments of pigments as substitutes), there can occur not only the n-type conductivity characteristic of metals, but also superconductivity and, in addition, that it can occur at temperatures substantially higher than room temperature. However, the synthesis of such molecules seemed to be an almost insoluble problem at that time; let us add that, according to theoretical considerations, a one-dimensional metallic state had to be very unstable, and molecules of the type proposed by Little can be regarded as quasi-one-dimensional (that is "as if they are" one-dimensional, since the thickness of the molecular chain cannot be equal to zero).

But is it possible to create Little's model by replacing the polymer chain with a system forming a molecular crystal? This question was raised by the members of the Institute of Chemical Physics when they decided to conduct their search among organic charge-transfer complexes and ion-radical salts. Semiconductors had already been found among these compounds, but the properties of such systems were practically unknown.

Analysis showed that the failures of researchers in their attempts to synthesize organic metals certainly were not accidental. The majority of solid organic compounds are dielectrics and, less frequently, semiconductors chiefly because individual particles in molecular crystals are bound with one another by relatively weak Van der Waals forces incapable of, so to speak, moving electrons from their long-occupied places in the molecules.

This conclusion made it possible to formulate the peculiarities which organic metals had to possess. Firstly, substances claiming the name of organic metals must have a maximally close packing characteristic of the traditional metals (as soon as the distances between the particles become substantially smaller than the Van der Waals distances, the binding energy will sharply increase among them). Secondly, the molecules of organic metals had to contain sufficiently extended conjugation systems. Thirdly, the system must contain a sufficient number of current carriers capable of moving along the conjugated bonds. And so, in the middle of the 1960s, the Institute of Chemical Physics started working intensively on the topic "studies in the area of potential organic superconductors".

Shortly after the beginning of these studies, we obtained quasi-one-dimensional charge-transfer organic complexes which behaved alternately as dielectrics and as conductors: at relatively high temperatures, these compounds were quasi-one-dimensional metals, and the metal became a superdielectric when the temperature dropped to a particular value. It was already the first important success.

However, the main problems of the new scientific direction became apparent rather rapidly. Of course, both their formulation, and approaches to their solution depended on the specialty of those who tried to solve them: they were physicists or theoretical chemists, experimental physicists or chemists specializing in synthesis. Specifically, the chemists were faced with a number of interrelated problems. Chemists had to learn:

to obtain compounds with metallic properties which would be stable at least in a limited temperature range;

to overcome theoretically predicted instability of the metallic state of real quasi-one-dimensional systems and to obtain organic metals retaining their properties down to the lowest temperatures;

to transform organic metals into organic semiconductors;

to transform organic metals into dielectrics and superdielectrics;

to transform organic metals to superconductors.

Apart from all these purely scientific problems, there was another problem, the last in succession but not in its significance: to find the ways of using organic metals for practical purposes. It is already possible to state now that all these problems are solvable.

How Metals Are Synthesized

In the course of the above investigations, not only compounds with metallic conductivity were obtained, but it was also possible to formulate general criteria which make it possible to plan the synthesis of organic metals.

Let us examine the main peculiarities of the structure of charge-transfer complexes. These complexes consist of interacting donors (D) and acceptors (A) of

electrons. As a result of such intermolecular interaction, the electron density is transferred, the length of the electron system is increased and, in the extreme case, there can occur strongly ionized compounds consisting of ion-radicals ($D^{\cdot+}$ and $A^{\cdot-}$), which are the above-mentioned ion-radical salts. Also close to this class are the ion-radical salts formed by the ion-radical and a common ion with an opposite charge (anti-ion X), for example, a cation-radical salt $D^{\cdot+}X^{-1}$. Both classes of the compounds are characterized by a structure in which its component both the donors and acceptors of electrons, are packed in piles or chains; such crystals are referred to as quasi-one-dimensional, meaning that the distance between the molecules in the pile is substantially smaller than the distance between the piles.

Only the regular piles in which molecules are at equal distances close to one another are suitable for obtaining metallic conductivity; the principle of the closest packing (characteristic for ordinary metals) is accomplished here in a quasi-one-dimensional variant. And if the molecules contain unpaired electrons, such a structure ensures a considerable overlapping of their orbitals, as a result of which the current is capable of running along the pile (chain).

However there is the danger that, instead of the regular structure, a structure might form (and forms most frequently) in which the donor and the acceptor are not separated but are in the same pile; in this case, metallic conductivity is not realized. It is possible to overcome this difficulty by reducing the interaction of the donors with the acceptors in order to make the interaction of the donors with donors and acceptors with acceptors competitive, for example, by changing either the dimensions of the counterion or the acceptor, or their shape. Since the components of the conducting pile (chain) must be situated at minimal distances from one another, this peculiarity of the structure of organic metal can be controlled, for example, by changing the size of the counterion or by increasing the pressure.

It is remarkable that the electron transfer from the donor to the acceptor must be only partial: for example, cation-radical salts in which a total electron transfer occurred turned out to be dielectrics, while compounds with a partial electron transfer are organic metals. This was shown theoretically by A. A. Innik, corresponding member of the USSR Academy of Sciences, and confirmed experimentally by Soviet, American and Japanese researchers.

At the present time, semiempirical rules have also been formulated which connect the oxidation-reduction potentials of the donor and the acceptor with their ability to serve as a basis for the synthesis of organic metals.

Not Only Conductors

All organic metals discussed above lost their conductivity after the temperature dropped to a particular limit: after that the compound became a dielectric. Is it possible then to obtain an organic metal which would be stable down to the lowest temperatures when superconductivity could develop?

Affirmative answer to this question was given by the results of studies conducted in the USSR at the Institute of Chemical Physics, as well in the U.S.A., on compounds of various types; undoubtedly, this was a great achievement. And a few

years ago a group of Danish and French researchers, using an electrochemical method, synthesized the first organic superconductors. They were compounds based on tetramethyl selenafulvalene (TMTSF) with a composition of $(\text{TMTSF})_2\text{X}$ where $\text{X} = \text{ClO}_4, \text{PF}_6, \text{AsF}_6, \text{TaF}_6, \text{SbF}_6, \text{FSO}_3, \text{ReO}_4$. At room temperature, the conductivity of these compounds is equal approximately to $400\text{--}800 \text{ Ohm}^{-1} \text{ cm}^{-1}$, and, as the temperature drops, it increases, reaching the value of $10^5 \text{ Ohm}^{-1} \text{ cm}^{-1}$ before the metal-dielectric transition. It was found that all compounds of this type, with the exception of perchlorate, undergo the metal-dielectric transition at temperatures from 12 to 180 K, but this transition is suppressed at an elevated pressure and in the region of 1-1.5 K the substances change to a superconducting state: however, perchlorate possesses superconducting properties even at the atmospheric pressure. It was noted also that pressure leads to an increase in the dimensionality of the system: its transformation from a quasi-one-dimensional to quasi-two-dimensional.

In the 1960s, many organic polymers containing branching systems of conjugated pi-bonds were synthesized. However, the conductivity of these polymers turned out to be low: in the majority of cases, they were either dielectrics or semiconductors. Only in 1977 fundamentally new results were obtained in the area of organic polymers: during the treatment of polyacetylene films with strong reducers or oxidizers (donors or acceptors of electrons), there occur dramatic changes in their conductivity. For example, if a cis-polyacetylene film is treated with sodium naphthalide, iodine, bromine or arsenic pentafluoride, its conductivity increases from $10^{-9} \text{ Ohm}^{-1} \text{ cm}^{-1}$ to $500 \text{ Ohm}^{-1} \text{ cm}^{-1}$. Thus, polyacetylene becomes a metal after a simple chemical operation. This is similar to the process when silicon or germanium acquire new electrophysical properties through alloying.

To date, organic polymers with a metal-like conductivity have been obtained on the basis of acetylene, benzene, pyrrole, thiophene and some other substances. The possibility of obtaining conducting films deposited on various surfaces (dielectrics, semiconductors, metals) is also of interest. For example, the Institute of Chemical Physics has developed a photoelectrochemical method for synthesizing alloyed pyrrole film deposited on semiconductors. It is also possible to deposit conducting films of polyacetylene on inorganic and organic conductors and dielectrics shaping them to various forms.

The new materials and the new possibilities connected with them are challenging traditional technologies. At the same time, it is possible to hope for the appearance of specific application areas of synthetic materials.

For example, there are more and more discussions today about the appearance of a new scientific and technical discipline, organic electronics, assuming that the electronics of the relatively near future will be using organic materials widely. Particularly attractive is the possibility of using organic compounds for creating information recording systems, sources of current, converters of the energy of solar light, antistatic coatings, and electrochromium devices.

It is important for technology that the majority of conducting polymers are very inexpensive (corresponding monomers are often products of the basic organic

synthesis), have a low density, and in many instances exhibit high corrosion resistance and plasticity. If we relate conductivity to a unit of weight, we will find that conducting polymers are not much behind metals possessing the highest electric conductivity.

Of course, we should not think that everything progresses smoothly in the creation and practical introduction of organic metals and that there are no problems or difficulties. Nevertheless, we can hope that in the near future very important results for practical applications will be achieved.

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CSO: 1841/121

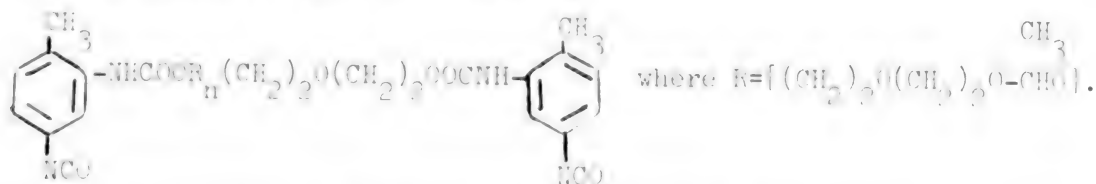
UDC 678.664:9.404

POLYACETALURETHANES: SYNTHESIS AND SELECTED PROPERTIES

Moscow KAUCHUK I REZINA in Russian No 12, Dec 83 (manuscript received 14 Jul 82)
pp 4-6

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[Abstract] A series of oligoacetals was synthesized which upon reaction with toluylenediisocyanate at 40-50°C in presence of a catalyst yielded oligoacetalurethanes (forpolymers) with the formula:



A method was developed for synthesis of oligoacetal vulcanizates by above reaction in presence of CaO; immediately after formation of the forpolymer it was solidified by trimerization using either an equimolar mixture of dimethylbenzylamine and phenylglycidyl ether or 4,4'-diamino-3,3'-dichlorodiphenylmethane. Thus-obtained polyacetalurethane exhibited satisfactory hydrolytic and thermal stability. Figures 3; references 5: 2 Russian (1 by Western authors) 3 Western.

[134-7813]

UDC 541.64:537.7

ELECTRICAL PROPERTIES OF PRODUCTS OF PYROLYSIS OF CARBORANE POLYARYLATES

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 1, Jan 84
(manuscript received 17 Feb 83) pp 704-707

VOISHCHEV, V. S., VALETERIY, F. M., BELOBLAZOV, V. A., GITSENKO, V. I. and
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[Abstract] Electrical spectroscopy was employed in the evaluation of the electrical conductivity of pyrolysis products obtained by thermal treatment of carborane polyarylates synthesized by the condensation of 1,7-bis-(4-phenylcarboxyphenyl)carborane with 4,4'-dihydroxydiphenyl ether in acetone with

triethylamine as accelerator. Films of the polymers were exposed to temperatures of 600, 900 or 1200°C for 1 h under a pressure of 10^{-3} torr, with temperature adjustment proceeding at a rate of 50°C/min. The heat-treated films retained their forms with insignificant shrinking; films exposed to 1200°C assumed a black metallic sheen. Heat treatment resulted, according to IR spectra, in extensive structural reorganization with the formation of thermally stable B-C and B-B bonds, with relatively insignificant mass loss (16% at 600°C, 23% at 900°C) at the lower temperature and no further mass loss at 1200°C. In addition, heat treatment increased the electrical conductivity measured at 150°C, which was most pronounced in the 900°C samples and represented a 12-order of magnitude greater value than of the untreated sample. An insignificant further increase in conductivity after heating at 1200°C suggested that in the 600-900°C range there were significant alterations in the internal structure of the polymer. Figures 2; references 9: 7 Russian, 2 Western. [141-12172]

TOP 341.04:06.17

EFFECT OF RED PHOSPHORUS ON THERMOXIDATIVE DEGRADATION OF α -CYANOPHOSPHAZINES

Moscow V.Y. KRAVCHENKO, L.Y. YAKOVLEV, S. YESTENENKO in Russian Vol. 17, No. 1, Jan. 82 (manuscript received 11 Dec. 81) pp. 50-53

KORSHAK, V. I., KRAVCHENKO, L. I., KRAVCHENKO, L. I., KAVIN, I. A. and KRAVCHENKO, L. I., Institute of Macromolecular Compounds named A. N. Seleznevskiy, USSR Academy of Sciences

[Abstract] Addition of finely dispersed red phosphorus to poly- α, α' -dicyanophenyl- α -cyanophosphazene- α, α' -dicarbonyl- α, α' -dicarbonyl was found to enhance its resistance to thermoxidative attack. Maximum resistance was obtained with red phosphorus added to a concentration of 1% by weight when heated for 1.5 h at 350°C, which was reduced to an oxygen index of 11.1 vs. 10.1 for the untreated α -cyanophosphazene polymer. Analysis of the IR spectra of untreated and treated samples indicated that red phosphorus catalyzes oxidation of the polymer, leading to the formation of a thermally stable structure with B-C-B bonds at a lower temperature than in the absence of phosphorus. This fact accounts for the almost equal index of the phosphorus-treated polymer and the increase in its autoignition point. Figures 3; references 4: 1 Russian, 3 Western. [141-12172]

EFFECTS OF STRUCTURAL HETEROGENEITY AND COMPOSITION ON ASSEMBLY OF PROTEIN MACROMOLECULES INTO GLASSY STATES

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 1, Jan 84
(manuscript received 29 Dec 82) pp 89-93

ASKADSKIY, A. A., KAZANTSEVA, V. V., BIKBOV, T. M., SLONIMSKIY, G. L. and KORSHAK, V. V., Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences

[Abstract] Studies were conducted on the coefficients of molecular packing of egg albumin, human serum albumin, lysozyme, and glycine achieved by compression at temperatures of 180-200°C. The data obtained by x-ray analysis, thermogravimetry and thermomechanical testing showed that the coefficient was within the range of 0.68-0.69 for the different proteins, and corresponded to the value for various glassy polymers. In this respect denatured proteins behave in a manner analogous to various synthetic polymers in that crystallization is independent of the chemical composition of the protein molecules. Figures 4; references 6: 5 Russian, 1 Western.
[141-12172]

UDC 541.64:547.954

SYNTHESIS AND CERTAIN CHARACTERISTICS OF POLYARYLENESULFONEOXIDE-POLYTETRAMETHYLENEOXIDE BLOCK COPOLYMERS

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 1, Jan 84
(manuscript received 31 Dec 82) pp 94-96

AKSENOV, A. I., STEROZHUK, I. P., AKSENOVA, T. S. and KORSHAK, V. V., Moscow Institute of Chemical Technology imeni D. I. Mendeleev

[Abstract] Description is provided of the synthesis of polyblock polyarylenesulfoneoxide-polytetramethyleneoxide block copolymers of variable compositions by the reaction of equimolar concentrations of oligoarylenesulfoneoxidediols and oligotetramethyleneoxidediols with 1,6-hexamethylene-diisocyanate for 4 h at 80°C in anhydrous chlorobenzene with 0.01 wt% tin diethyl caprylate. The resultant rigid blocks had molecular weights of 1600 and 4700, and the elastic blocks had molecular weights of 1000, 1500, and 2000. Physicochemical tests indicated that the block copolymers were highly resistant to deformation and tolerated temperatures of 210-230°C well. However, a 5% mass loss was noted at temperatures of 225-300°C. Figures 1; references 2: 3 Russian, 2 Western.
[141-12172]

SYNTHESIS AND CERTAIN CHARACTERISTICS OF POLYARYLENESULFONEOXIDE-POLYETHYLENEOXIDE BLOCK COPOLYMERS

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 1, Jan 84
(manuscript received 31 Dec 82) pp 97-103

AKSELEV, A. I., STOKOLZHIK, I. P., AKSENOVA, T. S. and KORSHAK, V. V., Moscow
Institute of Chemical Technology imeni D. I. Mendeleev

[Abstract] The synthesis of polyarylenesulfoneoxide-polyethyleneoxide block copolymers was achieved by reaction of the equimolar mixture of oligoarylene-sulfoneoxide-diol and oligoethyleneoxide-diol with 1,6-hexamethylenediisocyanate. The reactions were conducted for 4 h at 80°C in anhydrous chlorobenzene with 0.01 wt% tin diethyl caprylate, and the resultant block copolymers were precipitated with hexane and dried at 40°C. Evaluation of a large variety of such polymers demonstrated that their mechanical and chemical characteristics were predicated on their block composition and phase state. In general, they possessed excellent resistance to deformation and thermal resistance. In addition, block copolymers of the type investigated here are hydrophilic and, consequently, swell in water, and possess moderate antistatic properties. Figures 6; references 9: 5 Russian, 4 Western.
[141-12172]

STRUCTURAL CHANGES IN POLYAMIDES

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 1, Jan 84
(manuscript received 10 Jan 83) pp 104-110

KORSHAK, V. V., PAVLOVA, G.-S. A., GRIKOVA, P. N., POLINA, T. V. and
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[Abstract] Studies were conducted on structural changes and properties of aromatic polyamides stabilized with carbamate polyamides. Electron microscopy of the samples demonstrated that polyamides with up to 10% by weight of carbamate polyamide are morphologically homogeneous and do not differ from pure aromatic polyamide films both before and after thermal treatment at 270°C. This observation is taken as being indicative of the high degree of compatibility between the components in question. At any chosen ratio of components with a maximum of 50:50, thermal treatment results in the formation of a monophasic system due to their chemical reaction. In the case of the aromatic polyamides and carbamate polyamides the formation of the monophasic system evidently reflected formation of a copolymer. Figures 4; references 23: 21 Russian, 2 Western.
[141-13173]

SYNTHESIS AND STUDY OF CERTAIN POLYALKOXYPHOSPHAZENES

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 1, Jan 84
(manuscript received 25 May 82) pp 142-144

KIREYEV, V. V., BITTIROVA, F. A., MITROPOL'SKAYA, G. I., MIKITAYEV, A. K.,
PARKOV, V. S. and IL'INA, M. N., Moscow Institute of Chemical Technology imeni
D. I. Mendeleev; Institute of High Molecular Weight Compounds, Kabardino-
Balkar State University

[Abstract] Details are presented on the synthesis of poly-di-(n-hexyloxy)-
phosphazene (I), poly-di-(n-dodecyloxy)phosphazene (II) and poly-di-(n-octyl-
oxy)phosphazene (III), with data on their spectroscopic characteristics and
thermomechanical properties tabulated. These phosphazenes were found to be
inert in mineral acids and bases. Prolonged heating in the air under isothermal
conditions (140°C) shows a gradual mass loss and decrease in viscosity. Side
chains were determined to be in the most ordered form in II, and ordered to a
less rigid extent in I and III. The greatest resistance to stretch breaking
was shown by II (9.5 MPa) and III (10.0 MPa). Identity of the creep rates
obtained for I, II and III in various media was ascribed to the hydrophobic
nature of the alkyl side chains of these polymers. Figures 4; references 4;
3 Russian, 1 Western.
[141-14172]

OPTICALLY ACTIVE EPOXIDE POLYMERS: SYNTHESIS AND PREDICTION OF PHYSICAL
PROPERTIES

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 1, Jan 84
(manuscript received 12 Aug 83) pp 145-151

ASHANKELI, A. A., PASTERNOV, A. V. and NARSHALKOVICH, A. N., Moscow Engineering
and Construction Institute imeni V. V. Kuibyshev

[Abstract] Details are presented on the synthesis of a series of epoxide
polymers from epoxide oligomer ED-70, using iso-methyltetrahydrophthalic acid,
dicarboxylic azelaic acid or monocarboxylic oleic acid as curing agents, to
obtain optically-active model polymers suitable for experimental and mathemati-
cal characterization. Such optically-sensitive materials constitute ideal
objects for polarization methods of analysis of stress-induced deformations at
a given temperature, since their viscoelastic properties vary as the heating
temperature approaches the temperature of glassy transition (T_g). Thermo-
dilatometry, hydrostatic weighing and parameters of the lattice structure pro-
vided the data for mathematical analyses which demonstrated that the thermal
characteristics and T_g of the epoxide polymers can be predicted with consider-
able confidence. As the acid concentration of the polymers decreases, the

time required for equilibrium deformation varies; this fact accounts for the heterogeneous rheologic properties of these viscoelastic optically sensitive polymers. Figures 9; references 7 (Russian).
[141-12172]

UDC 541.64:547.4.03.01

CONTINUOUS METHOD OF PRODUCING CELLULOSE FIBER MATERIALS HAVING ANISOTROPIC PROPERTIES

Ivanovo IZVESTIYA VYSSHNIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNIKA in Russian Vol 26, No 4, Dec '83 (manuscript received 13 Apr 82)
pp 1432-1432

TERHAN', LE CHAU, ANTONIYAN, I. A., PETERENIK, M. A. and VETNIK, A. D.,
Department of Chemical Fibers Technology, Moscow Textile Institute imeni
A. S. Kosygin

[Abstract] A continuous method of synthesizing a graft copolymer of cellulose and N-(dimethylcarboxymethyl)-acrylamide (DDCM), initiating the graft polymerization reaction with the aid of an Fe^{2+}/H_2O_2

oxidation-reduction system in which the Fe^{2+} ions are bound with carboxylic groups of cellulose is described and discussed. Optimum conditions which prevent formation of a homopolymer of DDCM on fabric are presented. The reaction at 372 K in water vapor produces greater conversion of the monomer to the graft polymerization than the reaction at 242-250 K in an air-heated chamber. The rate of graft polymerization is greater when heating the fabric in a water vapor medium than when heating it in a heat chamber. The method can be employed in operative chemical fiber or textile shops. References: 3 (Russian).
[141-2771]

UDC 628.006.926

ACRYLAMIDE POLYMERIZATION IN PRESENCE OF AN ISOLATED METALLOPORPHYRIN

Ivanovo IZVESTIYA VYSSHNIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNIKA in Russian Vol 26, No 4, Dec '83 (manuscript received 14 Apr 82)
pp 1432-1432

POVARNY, V. I. and ALIFOVA, M. I., Chair of Organic and Physical Chemistry, Oryol State University imeni M. V. Lomonosov

[Abstract] A new approach has been developed for the immobilization of metalloporphyrins in hydrophilic polyacrylamide (PAA), in order to obtain efficient gel-immobilized catalytic systems. The essential feature consists of copolymerization of acrylamide, N,N-methyl methacrylamide and metalloporphyrins with one or two vinyl side groups, which results in the formation

complex with immobilized metalloporphyrin. The resultant polymeric metalloporphyrin complexes constitute efficient redox systems for initiating acrylamide polymerization in an aqueous medium, using hydrogen peroxide as a secondary component. No activity is seen during the first hour at 50°C, which apparently represents the time required for the diffusion of hydrogen peroxide to the metalloporphyrin centers. At 50°C the degree of polymerization of acrylamide approaches 50% in two hours, and diminished thereafter. Maximum activity in the polymerization of acrylamide was shown by the $\text{NiCl}_2(\text{P}(\text{O})\text{H}_2)_2$ system, and the least by the $\text{Co}(\text{Cl})_2(\text{P}(\text{O})\text{H}_2)_2$ system. Therefore, redox-immobilized metalloporphyrins constitute an efficient redox system in conjunction with hydrogen peroxide for controlled polymerization of vinyl monomers in an aqueous medium. References: 1 Russian, 2 Western.

[155-1775]

1967015:1:547:71.47

STABILIZATION OF METAL-ORGANIC COMPOUNDS IN POLYMERIZATION OF OLIGOMER, DIACRYLAMIDE OR A MIX OF ACCELERATED ELECTRONS AND IN STABILITY OF POLYMER COMPOUNDS WITH THESE OLIGOMER, DIACRYLAMIDE

Moscow INSTITUTE OF CHEMISTRY In Russian No 12, Dec 63 pp 1-7

POVIN, V. V., DEJINT, V. A., SHCHAYEVA, I. V., SYKHAROVA, V. A., SALAYEVA, V. Ye. and KUZNETSOVA, L. N.

[Abstract] Stabilization of bidimensional polymers is an unsolved problem. In the present paper results are reported on polymerization of oligomer compositions under action of accelerated electrons with addition of metal-organic compounds as stabilizers. It was shown that these additives have no effect on kinetic curves and the polymerization occurs almost quantitatively. This is due to specific characteristics of bidimensional polymerization in a flux of accelerated electrons. Polymer containing bidimensional stabilizers retains 100% stability during accelerated action in temperature range from -100°C to 100°C. Thus it was shown, that metal-organic compounds do not inhibit polymerization processes and can be used to produce bidimensional structures of polymers by the radiation method. References: 7 Western.

[153-7313]

PROPYLENE POLYMERIZATION ON TITANIUM-MAGNESIUM CATALYST

Moscow PLASTICHESKIYE MASSY in Russian No 12, Dec 83 pp 9-10

KASHIRINA, G. N., VOLOSHIN, I. A. and KRAVCHENKO, T. V.

[Abstract] Kinetics of propylene polymerization over the catalytic system titanium-magnesium (Ti-Mg) catalyst + triisobutyl aluminum + a modifier (p-methoxyethylbenzoate) was investigated. Optimal polymerization temperature for this system was 60°C. It was shown that Ti-Mg catalyst was much more active than the traditional catalyst, probably because of its higher number of active centers which result from structural binding of titanium tetrachloride to the magnesium chloride lattice. Molecular mass of the polymer was regulated by introduction of hydrogen into the reaction zone. With 10 vol-% of H₂ in the reaction zone, the maximum viscosity curve of the melted material was more slanting when Ti-Mg catalyst was used than with the commercial aluminum catalyst. Figures 2; references 8: 4 Russian, 4 Western (1 by Russian author). [108-7813]

POLYMERS BASED ON CYANOETHYLATED BIS-(CYANOAMIDES)

Moscow PLASTICHESKIYE MASSY in Russian No 12, Dec 83 pp 10-11

KORSHAK, V. V., SHUKUROV, G. I., PANKRATOV, V. A. and KUTEPOV, D. F.

[Abstract] Cyanoethylated bis-(cyanoamides) (I) were synthesized by the reaction of cyanoethylated diamines with cyanogen bromide in dimethylacetamide and the effect of the structure of starting monomers on thermal and physical and mechanical properties of resulting polymers was studied. It was found that even without a catalyst a polycyclotrimerization of I took place as low as at 343-393 K on account of the cyanamide groups; the nitrile groups were unaffected at this temperature. They appeared to partake in polymerization at temperatures ranging from 473 to 553 K. To lower polymerization temperature, various Lewis acids were tried and SnCl₂ appeared to be the most active.

Various glue compositions could be obtained using I giving material stable up to 523 K. Figure 1; references 3 (Russian). [108-7813]

SYNTHESIS OF PENTAPLAST USING ALUMINUMORGANIC CATALYSTS

Moscow PLASTICHESKIYE MASSY in Russian No 12, Dec 83 pp 12-13

IL'YASOVA, A. I., ISHMURATOVA, N. M., NIKITIN, V. S., SOMOVA, M. I.,
TOLSTIKOV, G. A. and SANGALOV, Yu. A.

[Abstract] Polymerization of 3,3-bis(chloromethyl)oxethane (BCMO) over higher aluminum organic compounds and alkylaluminum oxide leads to formation of high molecular products. The viscosity of polymer solutions and molten products of the materials obtained in the above process was investigated. In comparison to $\text{Al}(\text{iso-C}_4\text{H}_9)_3$, $\text{AlC}_{12}\text{H}_{21}$ type catalysts, which require higher temperature, result in higher solubility of the products. When epichlorohydrin was added, both $\text{Al}(\text{iso-C}_4\text{H}_9)_3$ and $\text{AlC}_{12}\text{H}_{21}$ type catalysts produced fully soluble fluid polymers. It was concluded that these catalysts should be recommended for syntheses of pentaplast because of their high activity, low content of impurities and low inflammability. Figures 2; references 4: 2 Russian, 2 Western.

[108-7813]

UDC 678.746.22(01+02):517.391+547.46

SYNTHESIS AND MODIFYING PROPERTIES OF GLYCIDIC ESTER OF 5-CHLORO-2-METHOXY-4-METHYL-4-PENTENIC ACID

Moscow PLASTICHESKIYE MASSY in Russian No 12, Dec 83 pp 13-15

AKHMEDOV, M. A., SADYKH-ZADE, S. I., KYAZIMOV, SH. K., AKHUNDOVA, R. I.,
BRUNO, V. V., KYAZIMOV, M. A. and VLADIMIROVA, I. I.

[Abstract] Synthesis of glycidyl ester of 5-chloro-2-methoxy-4-methyl-4-pentenic acid (I) was described. Condensation of metallyl chloride with trichloroacetaldehyde gave an unsaturated tetrachlorohydrin (II); hydrolysis-alcoholysis of II gave 5-chloro-2-methoxy-4-methylpentenic acid, which upon treatment with epichlorohydrin gave I, b.p. 140-142°C, n_D^{20} 1.4838, d_4 1.2065. Modification of an epoxide resin ED-20 with I gave epoxy compositions with improved physical-mechanical and dielectric properties in comparison with the starting FD-20 resin or ED-20 modified with TEG-1. Figure 1; references 4 (Russian).

[108-7813]

PRODUCTION OF CATION MEMBRANES BASED ON GRAFTED COPOLYMERS

Moscow PLASTICHESKIYE MASSY in Russian No 12, Dec 83 pp 15-16

TEVLINA, A. S., DEMIN, V. P. and CHELNOKOV, V. G.

[Abstract] Porous cation exchange membranes were obtained by chemical grafting of vinyl monomer (styrene on a copolymer of hexafluoropropylene and vinylidene fluoride) followed by introduction of ionogenic groups. The following compounds were used as pore-forming agents when ion exchange membranes were prepared: 3,3'-dimethoxybenzidine, p-toluidine, maleic acid, maleic anhydride, $PbCl_2$ and ammonium thiocyanate. Optimal electrochemical properties of the membranes were obtained when dimethoxybenzidine and NH_4SCN were used as the pore-forming agents. Static exchange capacity of the membranes increased with increased content of pore-forming agent. Porous membranes containing sulfo-groups in the main chain could be used in hyperfiltration processes of the electrolyte solution. Figure 1; references 10: 5 Russian, 5 Western.
[108-7813]

UDC 678.664:535

DISPERSING AND ABSORBING PROPERTIES OF FPU

Moscow PLASTICHESKIYE MASSY in Russian No 12, Dec 83 pp 16-18

GEYDUR, S. A., KARAPETYAN, O. O. and TRIZNO, M. S.

[Abstract] Results of experimental and theoretical investigations of optical spectra of foam polyurethane (FPU) were reported: coefficient of transmission, reflection, absorption and dispersion in the visible, far-UV and near-IR spectral ranges. A quantitative relationship was found between optical and morphologic parameters of the FPU macrostructure. It was shown to be possible to estimate some morphological parameters of foam plastics on the basis of optical measurements. On the basis of theoretical considerations it was concluded that models for the optics of light-dispersing media may be used in analysis of the optical properties of FPU as well as in practical engineering to control optical and morphological parameters of various materials for production of dispersion filters and lasers with diffuse reverse bond. Altering technical regimens for processing FPU and PU may lead to production of optical instruments with regulated properties. Figures 3; references 13: 12 Russian, 1 Western.
[108-7813]

PHYSICAL-MECHANICAL AND ELECTRIC PROPERTIES OF POLYIMIDE FILM BASED ON
TRICYCLO-[4,2,2,0^{2,5}]-DEC-7-EN-3,4,9,10-TETRACARBOXYLIC ACID DIANHYDRIDE AND
4,4'-DIAMINODIPHENYL OXIDE

Moscow PLASTICHESKIYE MASSY in Russian No 12, Dec 83 pp 20-21

ZHUBANOV, B. A., VOROB'YEV, V. D., ALMABEKOV, O. A., DOBROKHOTOVA, M. L.,
TANUNINA, P. M., KRAVTSOVA, V. D. and BEKMAGAMBETOVA, K. Kh.

[Abstract] Experimental results were reported of the investigation of physical-mechanical properties of a polyamide obtained in a two-stage polycondensation reaction of tricyclo-[4,2,2,0^{2,5}]-dec-7-en-3,4,9,10-tetracarboxylic acid dianhydride with 4,4'-diaminodiphenyl ester (I). The following parameters were investigated: breakdown stretching tension, relative elongation at the breaking point, tangent of the angle of dielectric losses, dielectric permeability, specific volume, electric resistance and electric charge. Polymer with characteristic viscosity $\eta = 1.4$ dl/g was used in these studies. Overall, it was shown that I exhibited excellent physical-mechanical and dielectric properties, making it an excellent candidate for electric insulating materials. Figures 2; references 10 (Russian).
[108-7813]

STUDY OF RADIATION ELECTROCONDUCTIVITY OF SOME POLYMERS

Moscow PLASTICHESKIYE MASSY in Russian No 12, Dec 83 pp 23-26

ALEKSANINA, O. S. and SICHKAR', V. P.

[Abstract] It was of interest to find out what effect will be manifested on σ_R (radiation electroconductivity) of polymer dielectrics after preliminary exposure to relatively low doses of Co⁶⁰ γ irradiation under conditions where σ_R is measured immediately after irradiation, or a short time afterwards. With this as a goal, radiation electroconductivity was studied of technical films of the following materials: high pressure polyethylene (PPPE), polypropylene (PP), polyethyleneterephthalate (PETP), polytetrafluoroethylene (PTFE), PVC and polystyrene (PS). PETP specimens, regardless of their thickness, showed a reversible decrease of absolute σ_R (2.5-3 fold) after preliminary irradiation. When the temperature was raised from 20 to 100°C, this effect disappeared. It was also shown that σ_R of a given material 20 min after preliminary irradiation was about 5 times higher than σ_R of the starting material; after one day storage, this value dropped down to the normal level. In PTFE, σ_R decreased

with increasing dose accompanied with changing Δ coefficient because of the reaction of radiolysis products created by preliminary irradiation with surrounding medium forming peroxide radicals which then participated in the capture-release process of quasi-free current carriers. Figures 5; references 7: 6 Russian (1 by Western author), 1 Western.
[108-7813]

UDC 678.744.335:678.346.22:678.743.22.02.01

GASPERMEABLE MATERIAL BASED ON PMMA, PS AND PVC

Moscow PLASTICHESKIYE MASSY in Russian No 12, Dec 83 pp 48-49

GOLUBEV, A. I.

[Abstract] The properties of compositions and solidified samples as well as physical principles of preparation of gas permeable materials were studied using water as the pore-forming agent. The following materials were investigated: components of plastic AST-7 consisting of a powder (a mixture of polymethylmethacrylate and benzoyl peroxide) and a liquid (a mixture of methylmethacrylate and dimethylaniline), PVC in suspension and emulsified polystyrene. A polymer paste capable of self setting at room temperature was prepared and after addition of PVC in forms of dry and wet powder it was left to set at room temperature. It was not possible to introduce water into the system without a hydrophilic filler (PVC). Wetted PVC distributed itself with ease in the polymer paste. Thus, uniformly distributed water facilitated uniform heat transfer during the polymerization process, speeded up the reaction and led to uniform pore formation. Reference 1 (Russian).
[108-7813]

UDC 678.048

POLYHEXAZOCYCLANES AS PHOTO- AND THERMOSTABILIZERS FOR POLYMERS

Moscow PLASTICHESKIYE MASSY in Russian No 12, Dec 83 pp 49-50

KALONTAROV, I. Ya., CHAYKO, Yu. V., NIYAZI, F. F., SILING, S. A. and PONOMARENKO, I. I.

[Abstract] Macroheterocyclic compounds have a high degree of unsaturation, making them interesting subjects for studying their photo- and thermostabilizing activity. The stabilizing activity of these polyhexazocyclanes was investigated on cellulose diacetate and polyamides exposed to UV irradiation of a full spectrum of a mercury-quartz lamp PRK-2 for 24 hrs. Stabilizing activity was determined by reduced viscosity of polymer solutions in dimethylformamide and formic acid. Thermal stability was studied by polymer destruction due to isothermal heating at 200°C for 6 hrs. It was shown that the polyhexazocyclanes were both photo- and thermally stabilizing agents for acetylcellulose materials. Figure 1; references 6 (Russian).
[108-7813]

REGULATION OF POLYETHYLENE STRUCTURE IN CAST PRODUCTS BY DOPING

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 274, No 1, Jan 84
(manuscript received 21 May 83) pp 144-148

SOYREF, D. A., ZUBOV, Yu. A., AKUTIN, M. S., ABRAMOV, V. V., CHVALUN, S. N.,
BAKEYEV, N. F. and VESELOV, A. V., Moscow Chemical and Technological Institute
imeni D. I. Mendeleev

[Abstract] Doping is a method of regulating the structure and properties of polymers by adding very small quantities of various substances, including polymers incompatible with the material being modified. Based on the example of a standard cast blade specimen of high density polyethylene, an estimate is made of the texture of polymer material crystals in the cast products. The influence of modification by adding small quantities of materials (up to 10%) on the structure of the polymer formed by casting under pressure is studied on the example of modification of high density polyethylene by a thermoelastoplast. The texture of the polyethylene was determined by x-ray studies. The fraction of oriented crystals of various types was determined to provide a quantitative estimate of the texture of the polymer in the product. The results indicated an increase in shear forces which develop in the mass of the polymer in comparison to a nonmodified polyethylene. The effective combined action of the modifier on the structure of the polymer being molded, resulting from nonadditive changes in rheologic and relaxation properties, is apparently the reason for the increase in durability characteristics of the products when doped with small quantities of thermoelastoplastic materials. Figures 2; references 15: 10 Russian, 5 Western.
[122-6508]

UDC 678.744.335:541.124.2:[547.841-39+546.732]

4-PHENYL-1,3-DIOXANE HYDROPEROXIDE AND COBALT CHLORIDE CYCLOHEXYL SULFOXIDE SYSTEM--EFFECTIVE METHYLMETHACRYLATE POLYMERIZATION INITIATOR

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 274, No 1, Jan 84
(manuscript received 13 Apr 83) pp 118-120

KURAMSHIN, E. M., D'YACHENKO, V. A., SHAUL'SKIY, Yu. M., ZLOTSKIY, S. S. and
RAKHMANKULOV, D. L., Ufa Institute of Petroleum

[Abstract] The authors determined for the first time that the hydroperoxide of cyclic acetals in the presence of cobalt (II) salts can initiate free radical processes such as polymerization under mild conditions. Studies were performed on 4-phenyl-1,2-dioxane hydroperoxide and cobalt chloride cyclohexyl sulfoxide with methymethacrylate monomer. Without the cobalt salt, 4-phenyl-1,3-dioxane hydroperoxide (PDHP) effectively initiates polymerization only at 70°C. Introduction of the cobalt salt catalyst significantly increases the speed of the process and allows it to be performed at 50°C in 5 hours rather than 30 hours. Figures 3; references 10 (Russian).
[122-6508]

CATALYTIC EFFECT OF COPPER ACETATE ON POLYMERIZATION OF STYRENE IN PRESENCE OF WATER

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 274, No 1, Jan 84
(manuscript received 21 Mar 83) pp 121-123

NIKOLAYEV, A. F., BELOGORODSKAYA, K. V., KRYZHANOVSKIY, A. V. and
SUVOROV, A. V., Leningrad Technologic Institute imeni Lensovet

[Abstract] The purpose of this work was to show that when the proper cocatalyst is used it is possible to initiate polymerization of styrene in the presence of significant quantities of water (an order of magnitude greater than the molar concentration of copper acetate). The EPR and PMR methods were used to study polymerization of styrene in a medium of carbon tetrachloride under the influence of copper (II) acetate and trifluoroacetic acid (TAA) as a cocatalyst. The concentration of water in all studies was 0.012 mol/l, copper acetate 0.0010 mol/l, TAA 0.100 mol/l, monomer 4.00 mol/l. At these concentrations of reagents neither copper acetate nor TAA alone caused polymerization, when simultaneously present, however, they did cause formation of polystyrene with a mean molecular mass of 65,000. PMR data confirmed that metal salts can have a direct catalytic effect in cationic polymerization of styrene in the presence of significant quantities of water if a cocatalyst such as TAA and the monomer interact through a stage of formation of a highly polarized intermediate compound, in this case diamagnetic dimer complexes. Figures 2; references 7: 6 Russian, 1 Western.
[122-6508]

UDC 541.64:539.55

EFFECT OF PARAMETERS OF RUBBER PHASE ON VISCOSITY PROPERTIES OF HIGH IMPACT POLYSTYRENE

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 25, No 12, Dec 83
(manuscript received 2 Apr 82) pp 2513-2518

NIKITIN, Yu. V., Okhtinskiy Scientific-Industrial Association "Plastpolimer"

[Abstract] A study of the effect of parameters of the rubber phase on the viscosity properties of the melt of high impact polystyrene showed that viscosity of the melt increased during a simultaneous decrease of its high elasticity. Existing model concepts concerning the viscoelastic behavior of the melts of homopolymers are used to interpret the effect of the structure and composition of the rubber phase on the viscosity properties of high impact polystyrene. Combined use of derived regression equations make it possible to determine optimum values of parameters of the rubber phase as a function of requirements for a given high impact polystyrene according to viscosity and viscoelastic properties of the melt. Figures 3; references 8: 6 Russian, 2 Western.
[103-2791]

STUDY OF EPOXY POLYMERS BASED ON RESORCINOL DIGLYCIDYL ETHER MODIFIED BY LOW-MOLECULAR RUBBER

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 25, No 12, Dec 83
(manuscript received 29 May 82) pp 2536-2540

KOCHERGIN, Yu. S., ASKADSKIY, A. A., ZAYTSEV, Yu. S., KULIK, T. A.,
VYSOTSKAYA, G. V. and VESELOVSKIY, R. A., Ukrainian Scientific Research
Institute of Plastics, Moscow Engineering Construction Institute imeni
V. V. Kuybyshev

[Abstract] Physical-chemical properties of epoxy polymers based on resorcinol diglycidyl ether modified by low-molecular polybutadiene rubber are described. Small additions of the rubber reduced the amount and rate of creep of the epoxy polymer somewhat. Modification of the epoxy polymers by the low-molecular rubber produced two-phase systems with a high degree of molecular incompatibility with a complex of good physico-mechanical properties. Figures 4; references 12: 7 Russian, 5 Western.
[103-2791]

RELATIONSHIP OF THERMAL STABILITY OF PARTIALLY FLUORINATED POLYMERS TO THEIR STRUCTURE

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 25, No 12, Dec 83
(manuscript received 14 Jun 82) pp 2575-2579

LOGINOVA, N. N., MADORSKAYA, L. Ya. and PODLESSKAYA, N. K.,
Okhtinskiy Scientific-Industrial Association "Plastpolimer"

[Abstract] Analysis and summary of data concerning the thermal stability of polyvinylidene fluoride and a copolymer of tetrafluoroethylene with ethylene of equimolar composition was carried out in order to explain the effect of the type of alternation of methylene and perfluoromethylene groups on the thermal stability of the macromolecule as a whole. It was found that thermal degradation of polyvinylidene fluoride at 548-723 K and 408-423 K involves two competing reactions, dehydrofluorination and depolymerization. It was assumed that disruption of the structure of the chain in both the polyvinyl fluoride and the copolymer may cause a transition from depolymerization to dehydrofluorination and the reverse. It was concluded that the basic factor determining thermal stability of polyvinyl fluoride and copolymer of tetrafluoroethylene with ethylene is the type of alternation of the methylene and perfluoromethylene groups which cause different process mechanisms to occur during thermal degradation of these polymers. Figures 2; references 13: 12 Russian, 1 Western.
[103-2791]

DISTRIBUTION OF CENTERS OF MECHANOEMISSION ON SURFACE OF STRAINED POLYMERS

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 25, No 12, Dec 83
(manuscript received 10 Jun 82) pp 2617-2621

ZAKREVSKIY, V. A. and PAKHOTIN, V. A., Physico-technical Institute imeni
A. F. Joffe, USSR Academy of Sciences

[Abstract] A single chamber, electrostatic, electron-optical transducer was used to obtain an image of the surface of polymer films (SKI polyurethane and SKI-3 polyisoprene) stretched in a vacuum at a constant rate. Photographing at five frames per second showed clearly pronounced emission images. Stretching was accompanied by disappearance of some centers of emission and appearance of others. A rapid increase and then a sudden decrease of both the number of centers and their clarity was typical of polyurethane while the number and clarity of emission centers increased throughout the period of stretching polyisoprene. The distribution patterns of emission centers on the polymer surface readily obtained by this method show the effectiveness of use of this method for studying the mechanism of breakdown of polymers. Figures 3; references 8: 6 Russian, 2 Western.
[103-2791]

RUBBER AND ELASTOMERS

RUBBER PRODUCTION MISMANAGEMENT

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 8 Jan 84 p 2

[Article by D. Melikov, Sumgait correspondent]

[Text] "At the present, the demand of the national economy for nitril rubbers is being fully satisfied. In these conditions, difficulties are occurring with the sale of SKN rubber, primarily rubber of the SK Sumgait Plant." These lines in a letter from the USSR Ministry of Oil Refining and Petrochemical Industry more clearly than anything characterize the situation which has developed at the Sumgait Synthetic Rubber Plant.

This is not only occurring with the sale of nitril rubber. Matters with the other product of the plant, nitril latex, are even worse.

Warehouses of the Sumgait plant are loaded with rubber and over-flowing with the latex supply. The large, almost half a kilometer in length, production either is just at a standstill or works episodically. Those working in this section often must hear this angry remark addressed to them: "You're a burden to the entire factory..."

And yet a completely different mood prevailed here 3 years ago, when at the expense of great efforts, the Sumgait citizens put out new nitril production ahead of schedule, and a small flask of the first latex was a most valued relic. More than 9.5 million rubles of capital investments were assimilated into the newly erected project. The best efforts of the plant were put into this--highly qualified engineers, technicians and operators. And now, as a matter of fact, the entire plant, the necessity of which was proven by national economic demands, suddenly has turned out to be "unnecessary". How could this have happened?

Today it is already difficult to determine who is really guilty of miscalculations. The production project was set up 20 years ago now, and the chain of cause and effect connections leads off to such obscure distances that the starting point of the conversation is lost and those responsible for decisions undertaken cannot be traced.

Understandably, the Sumgait citizens are not any the better for this. They just become skilled hands at one sort of latex and it is necessary to take it

out of production because the demand for it has been exhausted. The central board has already issued the command to stop production because there is no demand for it.

The same thing is happening with rubber. The initial plan for last year was reduced several times. Then, the strict order was received: "Do not exceed the fixed plan, there is plenty of rubber."

The plant workers were sent to the planners in the Voronezh affiliate "Giprokauchuka": they stirred up trouble, now let's all set things right. And then the institute director, G. Fil'chenko, sent out telegrams to "planned consumers". We shall print one of them: "To the director of the VPO [expansion unknown] "Soyuzshin", Mitrofan, and the assistant director of scientific work of the NIIShP [Scientific Research Institute of Tire Production], Sapronov. Your sector of industry has repeatedly informed us of your significant demand for this type of latex...We request that you accelerate your usage of latex in the tire industry..."

This exact telegram was sent to the managers of "Soyuzlegsnabsbytyr'e" of the Ministry of Light Industry, having reminded them that they promised to purchase, only for non-fabric materials, approximately 4000 tons of nitril latex this year, and at the end of the Five-Year Plan they requested more than 6000 tons. Similar reminders went to many other customers "on paper" of Sumgait latex.

However, there are also examples of another sort. The Institute of the VNII [All-Union Scientific Research Institute], of Roofing of the Ministry of Construction Materials Industry reports that a new highly-effective bituminous-latex emulsion material has been developed for them which meets present requirements for construction and conducting repair jobs. One of the main components of this material is Sumgait latex. The demand for it in 1984 is to be 1000 tons, and in 1985--3000. The institute requests that the possibility of supplying this production be confirmed.

In Sumgait, they rejoiced: a solid customer had been found. However, their joy was premature--the Soyuzglavrezinosnabsbyt planned, for 1984, only 200 tons of latex of the sort which was required for the new tire...

Well, as for nitril rubber, the SK Krasnoyarsk Plant, having increased its capacities, now fully guarantees its demand by the national economy. Thus, the necessity of Sumgait rubber has dropped off. The fact that when calculating the capacity of the new production, the actual demand for its production was not taken into consideration, was recognized at one of the meetings on this problem by the head engineer of the VPO "Soyuzkauchuk", V. Rabotnov.

I look around and think: really, was all of this built and formed into columns and pipe-lines for nothing? The plant recently got this word from the USSR Ministry of the Petroleum Refining and Petrochemical Industry. "With the goal of exploiting free facilities in manufacture of nitril rubber, we are working out the organization of output of those facilities for high-styrol rubbers which are in increased demand." Couldn't the ministry specialists have "worked out" this problem sooner?

UDC 621.892.82 + 678.019.253

EFFECT OF PLASTIC LUBRICANTS AND THEIR COMPONENTS ON CHANGES IN COMPOSITION
OF RUBBERS AND RESINS

Moscow KAUCHUK I REZINA in Russian No 12, Dec 83 (manuscript received 14 Jul 82)
pp 12-14

OGORODNIKOVA, G. F. and SINITSYN, V. V., Scientific Research Institute of
Rubber Industry

[Abstract] Swelling of nonpolar hydrocarbon, polysiloxane, butadiene-nitrile and fluorine-containing rubbers and resins was studied in plastic lubricants and in their dispersion media based on petroleum oils, polysiloxane and fluoro-organic liquids. This was of great interest because most of plastic lubricants are solidified organic liquids which are physically-active media capable of reacting with rubbers. It was shown that the interaction of rubbers with lubricants depended on chemical nature of the rubber and dispersion medium of the lubricant, especially their mutual affinity. The type and concentration of lubricant setting agents showed practically no effect on rubber swelling. The degree of rubber swelling in various plastic lubricants determines their utilization in contact with resins. References 8 (Russian).
[134-7813]

UDC 678.4.028:[678.742.2-945.245.32]:546.221

PROPERTIES OF RESIN AND RESIN MIXTURES BASED ON CHLOROSULFONATED POLYETHYLENE
WITH MAGNESIUM SULFIDE

Moscow KAUCHUK I REZINA in Russian No 12, Dec 83 (manuscript received 23 Sep 82)
pp 18-19

NOSNIKOV, A. F. and BLOKH, G. A., Dnepropetrovsk Institute of Chemical
Technology imeni F. E. Dzerzhinskiy

[Abstract] In an attempt to increase the stability of resinous mixtures based on chlorosulfonated polyethylene (CSPE) towards rubber scorching and to improve chemical stability of resins prepared from this rubber, the possibility of replacing magnesium oxide-resin mixture with magnesium sulfide containing highly active technical carbon was investigated. Experimentally-obtained resin mixtures exhibited low minimal viscosity and high resistance to scorching. Resins prepared from this material exhibited optimal level of crosslinking;

they were highly elastic and showed resistance to wear along with high chemical stability. In general, the use of magnesium sulfide, 2-mercaptoimidazoline and small amounts of technical carbon PMO-101N as a vulcanizing system for CSPE was preferable to the system consisting of magnesium oxide and resin. References: 5 (Russian).
[134-7813]

UDC 678.002.614:678.049.112

SYNTHESIS AND USE OF DIISOPROPYLNAPHTHALENE AS RUBBER PLASTICIZER

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA
TEKHNOLOGIYA in Russian Vol 26, No 9, Sep 83
(manuscript received 4 Jan 82) pp 1130-1132

POLYAK, M. A., CHEKANOVA, A. A., BYCHKOV, B. N. and ZAKHAROV, N. D., Chair of
Chemical Technology of Elastomer Processing, Yaroslavl Polytechnical Institute

[Abstract] Diisopropylnaphthalene (I) was synthesized by the alkylation of naphthalene by propylene catalyzed by aluminum chloride, in analogy to the alkylation of benzene as previously described [Bychkov, BN, et al., Kinetika i Kataliz, 14(6):1414, 1973]. The product, I, was tested for its usefulness as a plasticizer for the synthetic rubbers SKN-26M (butadiene-acrylonitrile) and SKD. Evaluation of the various mechanical and chemical parameters showed that, in general, I was much more effective in the case of SKN-26M than for SKD. Particularly noteworthy was the increase in resilience, resistance to tearing, and improved thermal stability of SKN-26M. Figures 1; references 2 (Russian).
[130-12172]

WATER TREATMENT

UDC 628.543.563:622.765:661.185

FLOTATION REMOVAL OF CYANIDE IONS FROM INDUSTRIAL WASTE WATERS

Moscow KOKS I KHIMIYA in Russian No 1, Jan 84 pp 54-55

YEVTYUGINA, I. M., Ural Polytechnic Institute imeni S. M. Kirov, DERBYSHEVA, Ye K. and KOPYTOVA, L. A., Eastern Scientific Research Institute of Coal Chemistry

[Abstract] Attempts were made at improving the flotation approach to removing cyanide ions from industrial waste waters produced by coke-tar chemical plants, since the commonly-employed techniques are relatively inefficient because the finely-dispersed $K_4[Fe(CN)_6]$ slurry fails to sediment. In the present study best results were obtained when the $CN^-:Fe^{2+}:Fe^{3+}$ ratio is 1:0.33:0.11. Comparison of the $CN^- + Fe^{2+}$ and the $CN^- + Fe^{2+} + Fe^{3+}$ systems showed that incorporation of the Fe^{3+} salt leads to the formation of large-particle mixed ferrocyanides that show relatively rapid settlement and, therefore, offer ease of removal. In the case of the former system the key difficulty lies in the removal of the finely dispersed ferrocyanides that fail to settle.
[144-12172]

UDC 662.74:628.543.563

CLARIFICATION OF CIRCULATING WATER AT GAS WORKS

Moscow KOKS I KHIMIYA in Russian No 1, Jan 84 pp 55-56

VORONINA, V. M., BURYAK, V. I. and TITOV, I. P., INUS [expansion unknown]

[Abstract] A coagulation method was tested for the clarification of the circulating water at the Angarsknefteorgsintez plant, since simple settling under gravity has been found to be ineffective. The concentration of particulate matter in the water ranges from 342 to 839 mg/liter, with the coarse and fine fractions partitioned as 76-94% and 6-24%, respectively. Addition of aluminum sulfate to a concentration of 150-650 mg/liter resulted in 75-85% clarification of water containing 1-2 mg/liter of polyacrylamide. It was also determined that a similar degree of clarification was obtainable by the addition of 4-40 ml/liter of waste water from an ethylbenzene plant which contained aluminum chloride, and mixing for 2-10 min. Figures 2; references 4 (Russian).
[141-12172]

PURIFICATION OF SEWAGE FROM ZINC USING ORGANOPHOSPHORIC COMPLEXONS

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 12, Dec 83 pp 722-723

ARSENOVA, L. D., ZEL'MANOVA, I. Ya., LATYSHEV, Yu. M., RUDOMINO, M. V. and PRUTIKOVA, N. I.

[Abstract] In this study an attempt was made to develop purification methods for sewage based on precipitation of the undesirable zinc with organophosphoric complexons such as nitrilotrimethylphosphonic acid (NTPA) and its trisodium salt (NaNTPA) as well as glycinebismethylphosphonic acid (GPA). Laboratory experiments showed that the extent of zinc precipitation depends on the complexon used and on pH of the sewage. Overall, it was concluded that the best results were obtained on neutral sewage using NTPA at a ratio of $\text{Zn:NTPA} = 3:1$. This method should find wide application in aniline dye industry. Precipitated sludge could be used in agriculture as an effective microfertilizer.

References 7 (Russian).

[120-7813]

MISCELLANEOUS

UDC 541.515

SPECIFICS OF EPR SPECTRA OF SUBSTITUTED ORTHOBENZOSEMIQUINOLATE ANTIMONY
DICHLORIDE COMPLEXES

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 274, No 1, Jan 84
(manuscript received 26 Apr 83) pp 133-137

CHEKALOV, A. K., PROKOF'YEV, A. I., KHODAK, A. A., BUBNOV, N. N.,
SOLODOVNIKOV, S. P. and KABACHNIK, M. I., academician, Institute of
Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow

[Abstract] A study is made of the EPR of complexes formed upon interaction of certain substituted orthobenzoquinones with antimony trichloride. Information is obtained on the structural specifics of the particles formed. It is suggested that paramagnetic chelate-structure complexes are formed in the reaction. Equivalence of chlorine atoms in the EPR spectra of the complexes indicates tetrahedral configuration with identical placement of chlorine atoms relative to the plane of the free radical ligand. The orthosemiquinolates complexes of antimony dichloride were obtained by interacting the initial benzoquinones with antimony trichloride in ampules used for EPR measurements, which were then evacuated. Figures 2; references 6 (Russian).

[122-6508]

UDC 666.266.5/9

INFLUENCE OF SILVER CONCENTRATION ON OPTICAL AND TECHNOLOGICAL PROPERTIES OF
LITHIUM-ALUMINUM-SILICATE LIGHT-SENSITIVE GLASS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 274, No 1, Jan 84
(manuscript received 9 Jul 82) pp 142-144

BEREZHNOY, A. I., BLINOV, V. A., KRASNIKOV, A. S., GLUSHKOV, Yu. I., and
BELOV, N. V., academician (deceased), Ryazan State Pedagogic Institute

[Abstract] The method of quantitative spectral analysis has been suggested for estimation of the concentration of silver, copper, gold and other light-sensitive metals in various stages of the process of production of photo-sitalls. Four standard specimens were prepared for this purpose with known silver concentration, determined chemically at 0, 0.04, 0.08 and 0.12 mass percent. The specimens studied had the following chemical composition, in mass percent: SiO_2 76, Al_2O_3 , Li_2O 12 and K_2O 4. The specimens were flat disks 8 mm

in diameter. The standard and test glasses were exposed to ultraviolet light for 60 minutes at 80°C, the latent image was developed at 500°C, 30 minutes. Spectroscopic studies were performed in the visible and near ultraviolet area. Spectral analysis was performed on a spherical lump of each specimen 2-4 mm in diameter using the silver line with wavelength $\lambda=3385$ Å for photometry. Spectral analysis showed the presence of Si, Al, Li, Ag, O₂ and a number of other elements in compounds. Luminescence studies showed that it was most intensive in specimens containing the greatest quantity of silver. The spectral method was also used to study the influence of silver concentration on transmission coefficient of the light-sensitive glass, which increased with increasing silver content. As the glass making temperature increased there was a decrease in content of silver from 0.18% at 1050°C to 0.11% at 1250°C. Heat treatment of glass thus causes volatilization of silver. Figures 4; references 5: 4 Russian, 1 Western.
[122-6508]

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